MODELLING OF NOVOLAC TYPE PHENOL-FORMALDEHYDE POLYMERIZATION

A Thesis Submitted
in Partial Fulfilment of the Requirements
for the Degree of

MASTER OF TECHNOLOGY

By

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to the

DEPARTMENT OF CHEMICAL ENGINEERING

INDIAN INSTITUTE OF TECHNOLOGY KANPUR

JANUARY, 1981

TO

MAA AND DEWTA

CERTIFICATE

This is to certify that the work 'Modelling of Novolac Type Phenol Formaldehyde Polymerization' has been carried out under my supervision and has not been submitted elsewhere for a degree.

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ACKNOWLEDGEMENT

I wish to thank my thesis supervisor Dr. Anil Kumar without whose constant guidence and much needed encouragement at the moments of despair and frustration, this work would have been incomplete. I also thank Dr. S.K. Gupta for his useful suggestions on several occasions. I will also like to thank Mr. T.R. Gupta for his typing of the manuscript and Mr. D.S. Panesa for drawing the figures.

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NOMENCLATURE

M_n	=	Number average molecular Weight
M_w	=	Weight average molecular Weight
O_e, O_e'	=	Ortho external sites
O_i	=	Ortho internal sites
p_e	=	para external sites
p_i	=	para internal sites
P_i	=	Polymer molecule of chain length i with no ($-CH_2OH$)
Q_i	=	Polymer molecule of chain length i with substituted CH_2OH
r	=	rate of reaction

Symbol

[ ]	concentration

ABSTRACT

The kinetic model for irreversible novolac type for phenol formaldehyde polymerization is presented and equations governing the molecular weight distribution MWD of the polymer formed for both batch and homogeneous continuous flow stirred tank reactors (HCSTR) have been derived. The set of non-linear differential equations for batch reactor is solved using Runge-Kutta method of order 4 and the set of non-linear algebraic equations for HCSTRs is solved with the help of Brown's algorithm which is found to be more efficient than Newton's method. A sensitivity analysis of different reaction parameters have been carried out and the reactivity of the para position was found to be an important factor affecting the MWD. The results for HCSTR have also been compared with those for batch reactors and the former is found to give polymer of lower average molecular weights having higher polydispersity index. A model for the reversible case is also presented.

CHAPTER 1

Introduction:

There are several classes of condensation polymerization systems where Flory's equal reactivity hypothesis does not hold good[2]. Formation of Novolac type phenol formaldehyde polymer is one of the commercially important systems.

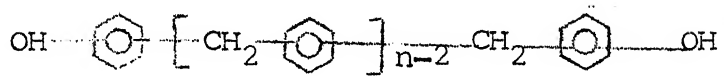
It is known that formaldehyde in water exists as methylene glycol ($OH - CH_2-OH$) and therefore exhibits a functionality of two. Phenol on the other hand has three reactive sites, two ortho positions and one para positions and experimental studies have shown that they have different reactivities[2,3]. Also the studies on gelations have revealed that the polymer molecules grow mainly by the reactions of the end groups. Drum and LeBlanc have explained this phenomena through molecular shielding assigning lower reactivities to internal sites.

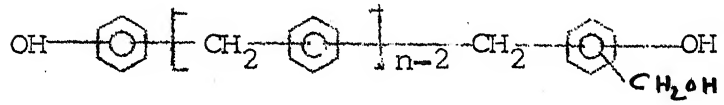
For polymerization systems where equal reactivity hypothesis holds, the expression for the reaction rate can be written in terms of reaction between functional groups. But in the case of novolac type polymerization one must write mass balance equations of individual polymer molecules of a given chain length in terms of reaction of these sites[1] and the resulting system of differential equations (including the balance equations of different sites) must be solved numerically for getting conversion and MWD.

CHAPTER 2

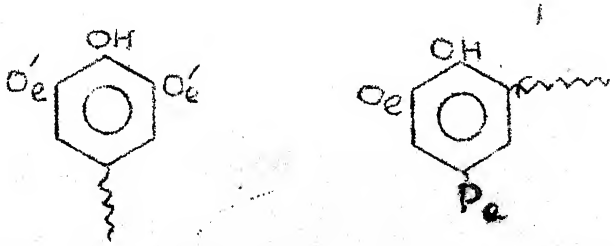
Kinetic Model:

In the reaction mass, the polymer chains are assumed to consist of all those molecules which have chain lengths greater than 2. There are two kinds of molecular species

P_n :  (a)

Q_n :  (b) (1)

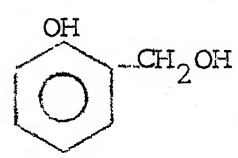
where the symbol  means that the bond formation has occured either at para or ortho position. The P_n and Q_n differ from each other only by substituted $-CH_2OH$. It is assumed that there is only one bound CH_2OH per chain which can be anywhere on it. These molecules contain external ortho (O_{eT}) and para position (p_e) which are present at chain ends and internal ortho and para positions (O_i and p_i) situated within the chain. All these positions have been shown to differ in their reactivities. The examination of chain ends reveals that the following two molecular structures can give rise to external ortho positions

 (2)

These are distinguished and denoted as O'_e and O_e. The total number of external ortho positions O_{eT}, is the sum of these two.

At a given time in the reaction mass, there can be free formaldehyde molecules and bound CH_2OH groups and the reactive sites can interact with both of these. The different reactions have been summarized in table 2.1. These reactions have been written to satisfy the site balance. As an example, reaction (a) table 2.1 stands for the fact that on reaction , O'_e, is assumed to be not available for further reaction which becomes O_i on further reaction. This fact has been represented by writing--O_e and + O_i in the right hand side. The reactivity of these reactions is assumed to be completely determined by the reactive sites involved in them. In reactions (a) to (e) of the table, the rate constants have been multiplied by factor 2 because in the formaldehyde molecules, there are two (OH) groups where the reaction can occur with equal likelihood.

The schematic reactions shown in Table 2.1 do not include these involving phenol. When phenol reacts with formaldehyde, it forms the following two species:

Q'_1 :  and Q_1 :  (3)

Reactions of Q_1 and Q_1' are also not covered by schematic equations of Table 2.1and they are all listed in Table 2.2. In reaction (a) of table 2.2 there are two positions on phenol (P) and two positions on F and therefore the reactivity has been shown to be $4k_1$ and so on. A mass balance on these species for batch reactors gives

$$\frac{d[O_e']}{dt} = -2k_1[O_e']\left[[Q_1] + 2[F] + [CH_2OH]\right] + [Q_1']\left[2k_1[O_e] + 2k_2[O_i] + 2k_3[P_i] + 2k_4[p_e] + 4(k_1+k_4)[P]\right] + \left[[Q_1] + [CH_2OH]\right] 2k_4 [P] \quad (4)$$

$$\frac{d[O_e]}{dt} = [Q_1]\left[k_1[O_e'] + k_2[O_i] + k_3[P_i] + (4k_1+k_4)[P]\right] - [Q_1'] \times \left[k_1[O_e] + k_4[p_e] - 2k_1[P]\right] - 2[F]\left[k_1[O_e] + k_4[p_e]\right] - [CH_2OH]\left[k_4[p_e] - 2k_1[P] + k_1[O_e]\right] \quad (5)$$

$$\frac{d[O_i]}{dt} = [Q_1]\left[k_1[O_e'] - k_2[O_i] + k_4[p_e]\right] + [Q_1']\left[k_1[O_e'] - k_2[O_i] + k_4[p_e]\right] + 2[F]\left[k_1[O_e'] - k_2[O_i] + k_4[p_e]\right] + [CH_2OH]\left[k_1[O_e'] - k_2[O_i] + k_4[p_e]\right] \quad (6)$$

$$\frac{d[P_i]}{dt} = k_1[O_e]\left[[Q_1] + [Q_1'] + 2[F] + [CH_2OH]\right] - k_3[P_i] \times \left[[Q_1] + [Q_1'] + 2[F] + [CH_2OH]\right] \quad (7)$$

$$\frac{d[P_e]}{dt} = [Q_1]\left[k_1[O_e'] + k_2[O_i] + (4k_1+k_4)[P] + k_3[P_i]\right] + [Q_1'] \times \left[2k_1[P] - k_1[O_e] - k_4[P_e]\right] - 2[F]\left[k_1[O_e] + k_4[P_e]\right] + [CH_2OH]\left[2k_1[P] - k_4[P_e]\right] \quad (8)$$

$$\frac{d[Q_1]}{dt} = 4k_1[F][P] - 2(k_1+k_4)[Q_1][P] - [Q_1]\left[k_1[O_e'] + k_1[O_e] + k_2[O_i] + k_3[P_i] + k_4[P_e]\right] - 2(k_1+k_4)[Q_1]^2 - (3k_1+k_4) \times [Q_1][Q_1'] - (k_1+k_4)[Q_1][CH_2OH] \quad (9)$$

$$\frac{d[Q_1']}{dt} = 2k_4[P][F] - (2k_1+k_4)[Q_1'][P] - [Q_1']\left[k_1[O_e'] + k_1[O_e] + k_2[O_i] + k_3[P_i] + k_4[P_e]\right] - 4k_1[Q_1']^2 - (3k_1+k_4)[Q_1] \times [Q_1'] - 2k_1[Q_1'][CH_2OH] \quad (10)$$

$$\frac{d[F]}{dt} = -2[F]\left[(2k_1+k_4)[P] + k_1[O_e'] + k_1[O_e] + k_2[O_i] + k_3[P_i] + k_4[P_e]\right] \quad (11)$$

$$\frac{d[P]}{dt} = -(2k_1+k_4)[P]\left[[Q_1] + [Q_1'] + 2[F] + [CH_2OH]\right] \quad (12)$$

Modelling of Molecular Weight Distribution:

In previous studies[1] it has shown that the concentration of bound CH_2OH in the reaction mass is small. In view of this, it is assumed that a polymer molecule in the reaction mass either has one bound CH_2OH or has none. In view of this, the growth of polymer molecules can be represented by following reactions:

$$P_n + F \longrightarrow Q_n \qquad (a)$$

$$Q_n + P_m \longrightarrow P_{n+m} \quad n,m = 2,3 \ldots \qquad (b) \qquad (13)$$

and

$$Q_n + Q_m \longrightarrow Q_{n+m} \quad n,m = 2,3 \ldots \qquad (c)$$

The reaction between Q_n and Q_m can occur in two ways:

(a) reactive sites on Q_n react with $(-CH_2OH)$ on Q_m

and (b) reactive sites on Q_m react with $(-CH_2OH)$ on Q_n

If o_eQ_n, o'_eQ_n o_iQ_n, p_iQ_n and p_eQ_n are total number of sites on all Q_n in the reaction mass and o_eQ_m, o'_eQ_m, o_iQ_m, p_iQ_m, and p_eQ_m on all Q_m in the system, the reaction rate, r_{mn} between Q_n and Q_m can be written as

$$r_{mn} = (k_1 o_e Q_n + k_1 o'_e Q_n + k_2 o_i Q_n + k_3 p_i Q_n + k_4 p_e Q_n)[Q_m]$$

$$+(k_1 o_e Q_m + k_1 o'_e Q_m + k_2 o_i Q_m + k_3 p_i Q_m + k_4 p_e Q_m)[Q_n]$$

$$m,n = 3,4 \qquad (14)$$

The above equation must be modified when either m or n is equal to 2

This is because polymer molecules of chain length 2 do not have internal sites and the above equation is modified to

$$r_{m2} = (k_1\, o_e\, Q_m + k_1 o'_e\, Q_m + k_2\, o_i Q_m + k_3 p_i Q_m + k_4 p_e\, Q_m)\ [Q_2]$$

$$+ (k_1\, o_e Q_2 + k_1 o'_e\, Q_2 + k_4 p_e\, Q_2)\ [Q_m] \quad m = 3,4 \qquad (15)$$

The reaction between Q_n and P_m, however, would not obey equations (13) and (14) because the bound CH_2OH of Q_n alone can react with reactive sites of P_m. Thus, the corresponding rate of reaction, r'_{mn}, can be written as

$$r'_{mn} = (k_1\, o_e P_m + k_1 o'_e\, P_m + k_2 o_i\, P_m + k_3\, p_i\, P_m$$

$$+ k_4 p_e\, P_m)\ [Q_n] \quad n = 2,3 \ldots\ldots$$

$$m = 3,4 \qquad (16)$$

When m = 2, the above equation must be modified to

$$r_{2n} = (k_1\, o_e\, P_2 + k_1\, o'_e\, P_2 + k_4 p_e\, P_2)\ [Q_n] \quad n = 2,3 \ldots \qquad (17)$$

To find $o_e\, Q_n$, it is noted that

$$o_e Q_n = [Q_n]\ (\text{Average fraction of sites on } Q_n \text{ that are } o_e) \qquad (18)$$

The fraction of sites on Q_n is assumed to be the same, on an average, as that of the overall average in the reaction mass. In other words,

$$o_e\, Q_n \simeq [Q_n]\ (\text{overall fraction of } o_e \text{ sites on all}$$

polymer molecules)

$$= [Q_n] \left\{ \frac{[O_e]}{\sum_2 [P_n] + \sum_2 [Q_n]} \right\} \qquad (19)$$

Following relations are written for other reactive sites as

$$O_e' Q_n = \frac{[O_e'] [Q_n]}{SUM} \qquad (a)$$

$$O_i Q_n = \frac{[O_i] [Q_n]}{SUM} \qquad (b)$$

$$P_i Q_n = \frac{[P_i] [Q_n]}{SUM} \qquad (c)$$

$$P_e Q_n = \frac{[P_e] [Q_n]}{SUM} \qquad (d) \qquad (20)$$

where

$$SUM = \left(\sum_2 P_n + \sum_2 Q_n \right) \qquad (21)$$

Similar relations are valid and can be written for $O_e P_n$, $O_e' P_n$ etc. In terms of these, equations (14) to (17) can be easily written as

$$r_{mn} = \frac{2\,CN}{SUM} [Q_m] [Q_n] \qquad (a)$$

$$r_{m2} = \frac{CN}{SUM} [Q_m] [Q_2] + \frac{CM}{SUM} [Q_m] [Q_2] \qquad (b)$$

q $$r'_{mn} = \frac{CN}{SUM} [P_m][Q_n] \quad (c)$$

$$r'_{2n} = \frac{CM}{SUM} [P_2][Q_m] \quad (d) \qquad (22)$$

where

$$CN = k_1[O_e] + k_1[O'_e] + k_2[O_i] + k_3[P_i] + k_4[P_e] \quad (a)$$

and $$CM = k_1[O_e] + k_1[O'_e] + k_4[P_e] \quad (b) \qquad (23)$$

Now one is in position to carry out the mass balance on P_n and Q_n which is done as follows. For the mass balance of Q_n it is noted that it is formed when P_n reacts with formaldehyde and Q_m reacts with Q_{n-m} where m could have any value between 1 and (n-1). Q_n is destroyed when it reacts with phenol or P_n and Q_m where m =2,3...., The balance for a batch reactor yields

$$\frac{d[Q_n]}{} = -(2k_1+k_4)[P][Q_n] - \left\{CN[Q_n] + \frac{CN}{SUM}[Q_n]\left(\sum'_{m=2}[Q_m] + [Q_1] + [Q'_1]\right) + (2k_1[Q'_1] + k_1[Q_1] + k_4[Q_i])[Q_n]\right\} + \frac{2\,CN}{SUM}[F][P_n]$$

$$+ \frac{CN}{SUM}\sum_{i=2}^{n-3}[Q_i][Q_{n-i}] + \frac{CM}{SUM}[Q_2][Q_{n-2}] + \frac{CN}{SUM}$$

$$[Q_1][Q_{n-1}] + (k_1+k_4)[Q_1][Q_{n-1}] + \frac{CN}{SUM}[Q_{n-1}][Q'_1]$$

$$+ 2k_1[Q'_1][Q_{n-1}] \quad n \geq 4 \qquad (24)$$

The relation above is valid for $n \geq 4$ and the balances for Q_2 and Q_3 are

$$\frac{d[Q_2]}{dt} = (k_1+k_4)[Q_1]^2 + 3(k_1+k_4)[Q_1][Q_1'] + 2k_1[Q_1']^2 + \frac{2\,CM}{SUM}[P_2][F]$$
$$-(2k_1+k_4)\left([Q_2][P] - CN[Q_2] - \frac{CM}{SUM}[Q_2]\left(\sum_2[Q_m] + [Q_1] + [Q_1']\right)\right)$$
$$-[Q_2]\,(2k_1[Q_1'] + k_1[Q_1] + k_4[Q_1]) \qquad (25)$$

and

$$\frac{d[Q_3]}{dt} = -(2k_1+k_4)[Q_3][P] - CN[Q_3] - \frac{CN}{SUM}[Q_3]\left(\sum_2[Q_m] + [Q_1] + [Q_1']\right) + \frac{2\,CN}{SUM}[P_3][F] + (k_1+k_4)[Q_1][Q_2] + 2k_1[Q_1'][Q_2]$$
$$+\frac{CM}{SUM}[Q_2]\,([Q_1] + [Q_1']) - (2k_1[Q_1'] + k_1[Q_1] + k_4[Q_1])[Q_3] \qquad (26)$$

On summation of equations (24) to (26), one obtains

$$\frac{d[-CH_2OH]}{dt} = \frac{d\sum_2^{\infty}[Q_n]}{dt} = -(2k_1+k_4)[P]\sum_{n=2}^{\infty}[Q_n] - CN\sum_{n=2}^{\infty}Q_n$$
$$+\frac{2[F]}{SUM}\left(CN\sum_{n=3}^{\infty}[P_n] + CM[(P_2]\right) + (k_1+k_4)[Q_1]^2$$
$$+(3k_1+k_4)[Q_1][Q_1'] + 2k_1[Q_1]^2 \qquad (27)$$

A smilar mass balance can be made on P_n. It is noted that P_n is formed when P_{n-1} reacts with Q_1 or Q_1' and P_{n-i} reacts w..h

Q_i. It is destroyed when it reacts with formaldehyde and any Q_m. The balance gives

$$\frac{d[P_n]}{dt} = \frac{CN}{SUM}[P_{n-1}]\left([Q_1] + [Q_1']\right) + \sum_{i=2}^{n-3} \frac{CN}{SUM}[P_{n-i}][Q_i]$$

$$+ \frac{CM}{SUM}[P_2][Q_{n-2}] + (2k_1+k_4)[P][Q_{n-1}] - \frac{2\,CN}{SUM}[P_n][F]$$

$$- \frac{CN}{SUM}[P_n]\left(\sum_{2}[Q_m] + [Q_1] + [Q_1']\right) \qquad n \geq 5 \qquad (28)$$

The above equation is valid only for $n \geq 5$ and therefore balances for P_2, P_3 and P_4 are written as

$$\frac{d[P_2]}{dt} = (2k_1+k_4)[P]\left([Q_1] + [Q_1']\right) - \frac{2\,CM}{SUM}[P_2][F]$$

$$- \frac{CM}{SUM}[P_2]\left(\sum_{2}[Q_m] + [Q_1] + [Q_1']\right) \qquad (29)$$

$$\frac{d[P_3]}{dt} = \frac{CM}{SUM}[P_2]\left([Q_1] + [Q_1']\right) + (2k_1+k_4)[P][Q_2] - \frac{2CN}{SUM}[P_3][F]$$

$$- \frac{CN}{SUM}[P_3]\left(\sum_{2}[Q_m] + [Q_1] + [Q_1']\right) \qquad (30)$$

$$\frac{d[P_4]}{dt} = \frac{CN}{SUM}[P_3]\left([Q_1] + [Q_1']\right) + \frac{CM}{SUM}[P_2][Q_2] + (2k_1+k_4)[P]$$

$$\times [Q_3] - \frac{2CN}{SUM}[P_4][F] - \frac{CN}{SUM}[P_4]\left(\sum_{2}[Q_m] + [Q_1] + [Q_1']\right)$$

(31)

To calculate the molecular weight distribution, eqns. (4) to (12) and (27) must be solved simultaneously and substituted in eqns. (24) to (28), to obtain $[P_n]$ and $[Q_n]$ as a function of time. These equations are written in dimensionless form using following variables.

$$Y_1 = \frac{[O_e']}{[F]_o} \qquad (a)$$

$$Y_2 = \frac{[O_e]}{[F]_o} \qquad (b)$$

$$Y_3 = [O_i] / [F]_o \qquad (c)$$

$$Y_4 = [P_i] / [F]_o \qquad (d)$$

$$Y_5 = [P_e] / [F]_o \qquad (e)$$

$$Y_6 = [Q_1] / [F]_o \qquad (f)$$

$$Y_7 = [Q_1']/ [F]_o \qquad (g)$$

$$Y_8 = [F] / [F]_o \qquad (h)$$

$$Y_9 = [P] / [F]_o \qquad (i)$$

$$Y_{10} = [CH_2OH] / [F]_o \qquad (j)$$

$$Y_{11} = [P_2] / [F]_o \qquad (k)$$

$$x = k_1 [F]_o t \qquad (l)$$

$$Y_{P_i} = [P_i] / [F]_o \quad i = 3,4 \qquad (m)$$

$$Y_{Q_i} = [Q_i] / [F]_o \quad i = 2,3..... \qquad (n)$$

$$R_1 = (k_2/k_1) \qquad (o)$$

$$R_2 = (k_3/k_1) \qquad (p)$$

$$R_3 = (k_4/k_1) \qquad (q)$$

Homogeneous Continous Flow Stirred Tank Reactor[4]

The rate equations derived for batch reactor can be incorporated in the steady state HCSTR simulation as follows:

Rate of input + Rate of generation due to reaction

= Rate of out put

For P_n and Q_n

$$v\,[P_n]_o + V\,(r_{P_n}) = v\,[P_n]$$

or

$$[P_n]_o - [P_n] + \tau \frac{d[P_n]}{dt} = 0$$

$$[Q_n]_o - [Q_n] + \tau \frac{d[Q_n]}{dt} = 0$$

where r_{P_n} = rate of formation of P_n

v = volume flow rate volume/time

V = volume of reactor volume

$[Q_n]_o$, $[P_n]_o$ = input concentration mole/volume

$[Q_n]$, $[P_n]$ = out put concentration mole/ volume

τ = residence time

Similar equations can be written for all the sites, P , F

Q_1 , Q_1' and Q_n . Thus we get a system of nonlinear algebraic equations. Since equation for $-CH_2OH$ is a dependent one, it is not incorporated. We get $-CH_2OH$ from the relation

$$[-CH_2OH] = \sum_{n=2}^{\infty} [P_n] + [Q_n]$$

The mole fraction distribution $MFDP_i$ and $MFDQ_i$ of species P_i and Q_i resepctively have been defined as

$$MFDP_i + = \frac{[P_i]}{\sum_{i=2}^{\infty} [P_i] + [P]} \qquad i=1,2,\ldots$$

$$MFDQ_i = \frac{[Q_i]}{\sum_{i=1}^{\infty} [Q_i] + [Q_1']} \qquad i=1,2,\ldots$$

In the above equation for n=1 in $MFDQ_i$, Q_{1T} is equal to (Q_1 + Q_1') has been used in the calculation.

In the weight fraction distributions, $WFDP_i$ and $WFDQ_i$, as opposed to this, the total weight of the reaction mass at the time of interest has been made as the basis as follows:

$$WFDP_i = \frac{WP_i}{\sum_{i=2}^{\infty} WP_i + \sum_{i=1}^{\infty} WQ_i + WP + WQ_1'}$$

and

$$WFDQ_i = \frac{WQ_i}{\sum_{i=2}^{\infty} WP_i + \sum_{i=1}^{\infty} WQ_i + WP + WQ_1'}$$

where WP_i, WQ_i, WP and WQ_1' refer to the weight of species P_i, Q_i, P and Q_1' respectively.

TABLE 2.1

Reactions of O_e, O_e', P_i, O_i and P_e

(1) With formaldehyde

$$O_e' + F \xrightarrow{2k_1} (-CH_2OH) + O_i - O_e' \quad (a)$$

$$O_e + F \xrightarrow{2k_1} (-CH_2OH) + P_i - P_e \quad (b)$$

$$O_i + F \xrightarrow{2k_2} (-CH_2OH) \quad (c)$$

$$P_i + F \xrightarrow{2k_3} (-CH_2OH) \quad (d)$$

$$P_e + F \xrightarrow{2k_4} (-CH_2OH) + O_i - O_e \quad (e)$$

(2) With bound formaldehyde ($-CH_2OH$)

$$O_e' + (-CH_2OH) \xrightarrow{k_1} O_i - O_e' \quad (f)$$

$$O_e + (-CH_2OH) \xrightarrow{k_1} P_i - P_e \quad (g)$$

$$O_i + (-CH_2OH) \xrightarrow{k_2} \text{consumption} \quad (h)$$

$$P_i + (-CH_2OH) \xrightarrow{k_3} \text{consumption} \quad (i)$$

$$P_e + (-CH_2OH) \xrightarrow{k_4} O_i - O_e \quad (j)$$

TABLE 2.2

Reactions of P, Q_1 and Q_1'

(a) Reactions of P with F and $(-CH_2OH)$

$$P+F \xrightarrow{4k_1} Q_1 \quad (a)$$

$$P+F \xrightarrow{2k_4} Q_1' \quad (b)$$

$$P+(-CH_2OH) \xrightarrow{2k_1} p_e + o_e \quad (c)$$

$$P+(-CH_2OH) \xrightarrow{k_4} 2\,o_e' \quad (d)$$

(b) Reactions of P with Q_1 and Q_1'

$$P + Q_1' \xrightarrow{2k_1} p_e + 2o_e' + o_e \quad (e)$$

$$P + Q_1' \xrightarrow{k_4} 4\,o_e' \quad (f)$$

$$P + Q_1 \xrightarrow{2k_1} 2p_e + 2o_e \quad (g)$$

$$P + Q_1 \xrightarrow{k_4} o_e + P_e + 2o_e' \quad (h)$$

(c) Reactions of Q_1 and Q_1' with reactive sites

$$o_e' + Q_e' \xrightarrow{k_1} o_i + 2o_e' - o_e' \quad (i)$$

$$o_e' + Q_1 \xrightarrow{k_1} p_e + o_e + o_i - o_e' \quad (j)$$

$$o_e + Q_1 \xrightarrow{k_1} p_e + o_e + p_i - p_e \quad (k)$$

$$o_e + Q_1' \xrightarrow{k_1} 2o_e' + p_i - p_e \quad (l)$$

$$p_i + Q_1 \xrightarrow{k_3} O_e + p_e \qquad (m)$$

$$p_i + Q_1' \xrightarrow{k_3} 2O_e' \qquad (n)$$

$$O_i + Q_1' \xrightarrow{k_2} 2O_e' \qquad (q)$$

$$O_i + Q_1 \xrightarrow{k_2} O_e + p_e \qquad (r)$$

$$p_e + Q_1 \xrightarrow{k_4} O_i + O_e + p_e - O_e \qquad (s)$$

$$p_e + Q_1' \xrightarrow{k_4} O_i + 2O_e' - O_e$$

CHAPTER 3

NUMERICAL SOLUTIONS

1. Runge Kutta Method of Order 4:

The system of nonlinear differential equations for the batch reactor are solved in DEC 1090 computer using Runge Kutta Method of order 4. After a few trial, the stable solution was found for $x = 10^{-3}$. The algorithm of the technique is as follows[6]:

For the equation

$$y_1' = f_1 (x_1, x_2, x_3, \ldots\ldots, x_n)$$

$$y_2' = f_2 (x_1, x_2, x_3, \ldots\ldots, x_n)$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

$$y_n' = f_n (x_1, x_2, x_3, \ldots\ldots, x_n)$$

with $\bar{y}\ (\bar{x}_0) = \bar{y}_0$ where the bar indicates array gnerate approximations $\bar{y}_n$ to $\bar{y}\ (\bar{x}_0 + n \Delta x)$ for Δx fixed and for n n=0,1,2,.... using recursion formula

$$\bar{y}_{n+1} = \bar{y}_n + \frac{1}{6} (k_1 + 2k_2 + 2k_3 + k_4)$$

where

$$k_1 = x\ f\ (\bar{x}_n)$$

$$k_2 = x\ f\ (\bar{x}_n + \frac{\Delta x}{2})$$

$$k_3 = x\ f\ (\bar{x}_m + \frac{\Delta x}{2})$$

$$k_4 = x\ f\ (\bar{x}_n + \Delta x)$$

2. Brown's Method[5]:

The following system of nonlinear algebraic equations is considered

$$\begin{aligned} f_1(\bar{x}) &= f_1(x_1, x_2, \ldots, x_N) = 0 \\ f_2(\bar{x}) &= f_2(x_1, x_2, \ldots, x_N) = 0 \\ &\cdots \\ f_N(\bar{x}) &= f_N(x_1, x_2, \ldots, x_N) = 0 \end{aligned} \tag{3.1}$$

which can be written in vector form as $\bar{f}(\bar{x}) = \bar{0}$.

It is assumed that f_i are continuously differentiable. In Newton Raphson technique the functions in equations 3.1 are expanded about a point $\bar{x}^n$ which is close to the solution $\bar{x}^*$ yielding

$$\bar{f}(\bar{x}) = \bar{f}(\bar{x}^n) + J(\bar{x}^n) \cdot (\bar{x} - \bar{x}^n) + \text{H.O.T.} \tag{3.2}$$

where the higher order terms (H.O.T.) are negligible and only the first order terms are included. Since $\bar{x}^n$ are close to $\bar{x}^*$ one therefore has

$$\bar{f}(\bar{x}) = \bar{0} \quad \text{or} \quad \bar{0} - \bar{f}(\bar{x}^n) + J(\bar{x}^n) \cdot (\bar{x} - \bar{x}^n)$$

Solving for $\bar{x}$ gives

$$\bar{x}^{n+1} = \bar{x} = \bar{x}^n - J^{-1}(\bar{x}^n) \cdot \bar{f}(\bar{x}^n) \tag{3.3}$$

The solution procedure would therefore be the following:

Begining with a starting guess, $\bar{x}^0$ one solves equations 3.3 iteratively for n= 0,1,2,.... This can be done only when $J(\bar{x})$

is non-singular in a suitable neighbourhood of $\bar{x}^*$. A derivative free analogue of Newton's method often called the discrete Newton's method is obtained from equation 3.3 by replacing the ith row and jth column entry of the Jacobian matrix (i.e. $\frac{\partial f_i}{\partial x_j}$) by the first difference quotient approximation

$$\frac{f_i(\bar{x}^n + h^n \bar{e}_j) - f_i(\bar{x}^n)}{h^n} \qquad (3.4)$$

Here $\bar{e}_j$ denotes the jth unit factor and scalar h^n is normally chosen such that $h^n = O(\|f(\bar{x}^n)\|)$.

Brown technique calls the functions of equation 3.1 one at a time so that information obtained from working with f_1 can be incorporated in while working with f_2, etc. A successive substitution scheme is used rather than the simultaneous treatment of the f_i, as done in Newton's method. The former method is derivative free and its second order convergence has been proved. The method consists of applying the following steps:

Step 1:

Let $\bar{x}^n$ denote an approximation to the solution $\bar{x}^*$ of 3.1. The first function f_1 is expanded in an approximate Taylor series expansion about the point $\bar{x}^n$. By approximate it is meant the expansion in which the actual (analytic) partial derivatives are replaced by first difference quotient approximation.

$$f_1(\bar{x}) = f_1(\bar{x}^n) + f_{1x_1;h}(\bar{x}^n) \cdot (x_1 - x_1^n) + f_{1x_2;h}(\bar{x}^n) \cdot$$

$$(x_2 - x_2^n) + \ldots\ldots + f_{1x_n;h}(\bar{x}^n) \cdot (x_N - x_N^n) \qquad (3.5)$$

Here $f_{1x_j;h}(\bar{x}^n)$ is defined to be the first difference quotient approximation 3.4 with i=1. If $\bar{x}^n$ is close enough to $\bar{x}^*$, $f_1(\bar{x}) \simeq 0$ and equation 3.5 is equated to zero and solved for that variable, say x_N, whose corresponding approximate partial derivative, $f_{1x_N;h}(\bar{x}^n)$ is the largest in absolute value. This gives

$$x_N = x_N^n - (f^n_{1x_j;h}/f^n_{1x_N;h}) \cdot (x_j - x_j^n) - f_1^n/f^n_{1x_N;h} \qquad (3.6)$$

where $f_{1x_j;h} = f_{1x_j;h}(\bar{x}^n)$ as given in 3.4 and $f_1^n = f_1(\bar{x}^n)$. The constants $f^n_{1x_j;h}/f^n_{1x_N;h}$ are saved (stored) in the computer implementation of the algorithm for future use. By choosing the approximate partial derivatives of the largest value to divide by a partial pivoting effect is achieved, similar to what is often done when using the Gaussian elimination process for solving linear systems. This enhances the numerical stability of the method. It is observed from equation 3.6 that x_N is a linear function of the N-1 variables $x_1, x_2, \ldots x_{N-1}$ and for the purpose of clarity, the left hand side of 3.6 is redefined as

$L_N(x_1, x_2, \ldots x_{N-1})$ and define $L_N^n = L_N(x_1^n, x_2^n, \ldots x_{N-1}^n)$

Step 2:

Now a new function g_2 of N-1 variables $x_1,\ldots,x_{N-1}$ is redefined which is related to the second function f_2 of equation 3.1 as

$$g_2(x_1,\ldots,x_{N-1}) = f_2\ (x_1,\ldots,x_{N-1},\ L_N(x_1,\ldots,x_{N-1})) \quad (3.7)$$

Let g_2^n be defined as $g_2^n = f_2\ (x_1^n,\ldots,x_{N-1}^n,\ L_N^n)$. Now g_2 is expanded in an approximate Taylor series expansion about the point $(x_1^n,\ \ldots x_{N-1}^n)$, linearized (ignoring higher order terms) and solved for that variable, say x_{N-1}, whose corresponding approximate partial derivative $g_{2x_{N-1};h}$ is largest in mangnitude,

$$x_{N-1} = x_{N-1}^n - \sum_{j=1}^{N-2} (g_2^n\ x_j;h / g_{2x_{N-1};h}^n)\cdot (x_j - x_j^n) - g_2^n / g_{2x_{N-1};h}^n \quad (3.8)$$

Here the approximate partial derivative $g_{2x_j;h}^n$ is given by

$$g_{2x_j;h}^n = \frac{g_2(x_1^n,\ldots,x_{j-1}^n,x_j^n + h^n,x_{j+1}^n,\ldots,x_{N-1}^n) - g_2^n}{h^n} \quad (3.9)$$

where h^n is a small positive number. From equation 3.8 it is noted that x_{N-1} is a linear function of the remaining N-2 variables and it is denoted by $L_{N-1}(x_1,\ldots,x_{N-2})$. Again the ratios $g_{2x_j;h}^n / g_{2x_{N-1};h}^n$, $j=1,\ldots,N-2$ and $g_2^n / g_{2x_{N-1};h}^n$ are stored for future use.

Step 3:

One defines

$$g_3(x_1,\ldots,x_{N-2}) = f_3(x_1,\ldots x_{N-2}, L_{N-1}, L_N) \qquad (3.10)$$

with the argument of L_{N-1} being $(x_1,\ldots,x_{N-2})$ and the argument of L_N being

$$x_1,x_2,\ldots,x_{N-2}, L_{N-1}(x_1,x_2,\ldots,x_{N-2}) \qquad (3.11)$$

One carries out 1) approximate Taylor expansion of the function g_3 about $(x_1^n,\ldots x_{N-2}^n)$ followed by 2) linearization of the resulting expansion followed by 3) equating to zero and solving for one variable, say x_{N-2} (whose corresponding approximate partial derivative $g_{3x_{N-2};h}$ is largest in magnitude) as a linear combination L_{N-2}, of the now remaing N-3 variables. It is continued in this fashion, eliminating one variable for each equation treated. Every time a new linear expression, L_{N-k}, for one of the variables, say x_{N-k}, is obtained in terms of the remaining N-k-1 variables, $x_1,x_2,\ldots x_{N-k-2},x_{N-k-1}$. This linear expression is used whereever x_{N-k} had appeared in the previously defined linear expressions L_{N-k+1}, $L_{N-k+2}\ldots L_N$. It may be noted that each step in the alogrithm adds one more linear expression to a linear system. During the k+1 st step of algorithm, it is necessary to evaluate g_{k+1} i.e. f_{k+1}, for various arguments. The values of the last k components of the argument of f_{k+1} are obtained by back substitution in the linear system $L_N, L_{N-1}\ldots L_{N-k+1}$

which has already been found. The points which are back substituted consist of the point $(x_1^n,\ldots,x_{N-k}^n) = \bar{x}_{N-k}^n$ together with the points $x_{N-k}^n + h^n\bar{e}_j$, $j=1,\ldots,N-k$, where $\bar{e}_j$ denoted the jth unit vector. The arguments are required to determine the quantitities g_{k+1}^n and $g_{k+1,j;h}^n$, $j=1,\ldots,N-k$, needed for the elimination of the k+1 st variable: say x_{N-k}, by the basic processes of expansion, linearization and solution of the resulting expression. This process results for each k, in the k+1 st variable, say x_{N-k}, being expressed as linear combination L_{N-k} of the remaining N-k-1 variables.

Step N:

In the last step

$g_N = f_N(x_1, L_2, L_3\ldots, L_N)$ where L_j's are obtained by back substitution in the N-1 rowed trangular linear system which now has the form

$$L_i = x_i^n - \sum_{j=1}^{i-1} (g_{N-i+1,x_j;h}^n / g_{N-i+1,x_i;h}^n \cdot (L_j - x_j^n) - g_{N-1+1}^n / g_{N-i+1,x_i;h}^n, \quad i=N,N-1,\ldots 2 \qquad (3.12)$$

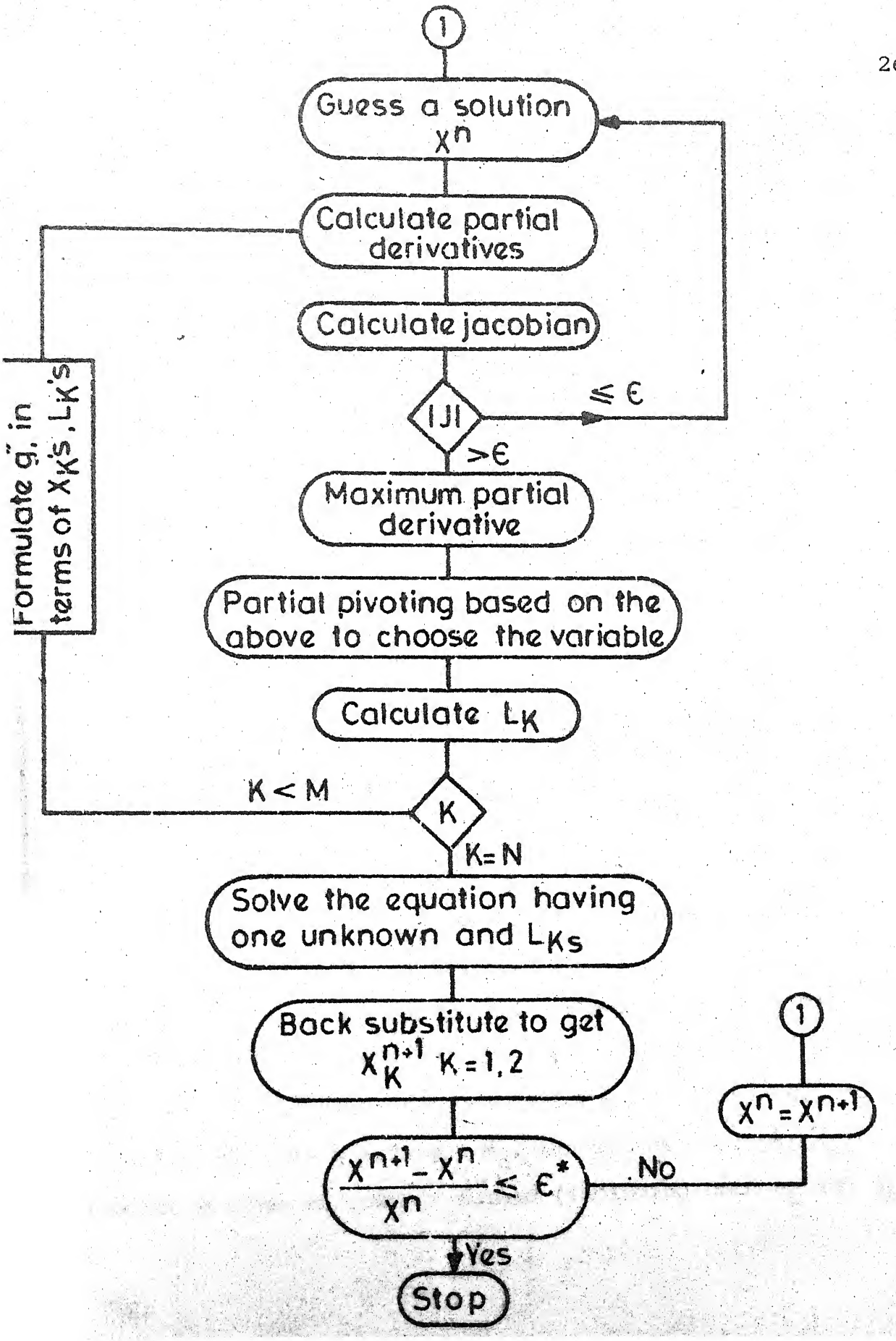
with $g_1 = f_1$ and $L_1 = x_1$) so that g_N is just a function of the single variable x_1. Now expanding, linearizing and solving for L_1, one obtains

$$x_1 = x_1^n - g_N^n / g_{N,x_1;h}^n$$

This point x_1 thus obtained is used as the next approximation,

x_1^{n+1}, two the first component x_1^*, of the solution vector $\bar{x}^*$. x_1 is renamed as L_1 and the L_j system in equation 3.12 is solved to get improved approximations of other components of $\bar{x}^*$.

The successive substitution nature of the algorithm allows the most recent information available to be used in the construction of the next function argument similar to what is done in the Gauss-Seidel process for linear and nonlinear systems of equations. A, simplified flow chart of the Brown's method is shown in figure 3.1


1
Guess a solution X^n
Calculate partial derivatives
Calculate jacobian
|J|
$\leq \epsilon$
$> \epsilon$
Maximum partial derivative
Partial pivoting based on the above to choose the variable
Calculate L_K
K
$K < M$
Formulate $\tilde{q}_i$ in terms of X_K's, L_K's
$K = N$
Solve the equation having one unknown and L_Ks
Back substitute to get X_K^{n+1} $K = 1, 2$
$\frac{X^{n+1} - X^n}{X^n} \leq \epsilon^*$
No
1
$X^n = X^{n+1}$
Yes
Stop

CHAPTER 4

RESULTS AND DISCUSSION

The mass balance equations for both batch as well as HCSTR are solved numerically in a DEC-1090 computer to examine the effects of various system parameters on molecular weights and conversions.

In figure 4.1 and 4.2 the mole fraction distributions (MFD) of P_i and Q_i have been plotted for different residence times of polymerization in HCSTR. On the same graph, the corresponding results for batch reactors have been given for comparison. As the time of polymerization increases, the distributions are found to become broader. For any given x, the conversion of phenol is always lower and $[Q_{1T}]$ $(= [Q_1] + [Q_1']$ is higher for the HCSTR. In view of lower conversion of phenol, the concentration of higher homologs are naturally lower than those obtained in batch reactors. In figure 4.3 and 4.4, the corresponding weight fraction distributions (MWD) for HCSTRs as well as batch reactors are given. The distribution for batch reactors in figure 4.3 undergoes a maximum at n=2 for residence times beyond x=0.3, whereas no such behaviour is seen for HCSTRs. The distribution curves for P_i as well as Q_i for HCSTR's are always found to be lower than those for batch reactors. In figure 4.5 the number average, $\bar{M}_n$, and weight average, $\bar{M}_w$, molecular weights of polymer formed (including both P_i and Q_i)

in the reaction mass for batch as well as HCSTRs has been plotted as a function of time. As expected, $\bar{M}_n$ and $\bar{M}_w$ for the latter are always found to be lower; however the polydispersity index, $\int$, for HCSTR is larger.

In figure 4.6 and 4.7, the effect of R_3 on the mole fraction distribution of P_i and Q_i at dimensionless residence time x=0.9 has been examined. In figure 4.6 for a given R_3, the distribution of P_i falls monotonically and beyond n=10, it is almost zero and as R_3 is increased, it becomes slightly broader. As can be seen from the figure the effect of R_3 on the MWD of the polymer from batch reactors, in contrast to this, is found to be much more. In figure 4.7 the effect of R_3 on the mole fraction distribution of Q_i has been shown. $[Q_{1T}]$ $(= [Q_1] + [Q_1'])$ for HCSTR is found to be much longer than for batch reactor, whereas the remainder of the distribution curve is found to be negligibly affected.

In figure 4.8 and 4.9, the effect of R_3 on $\bar{M}_n$ and $\bar{M}_w$ versus time has been examined. As R_3 increases, the $\bar{M}_n$ curves rise upwards; however for a given R_3 they are always lower than those for batch reactors. It can be noted that for large R_3, the reaction at para positions occur with higher likelihood, this way the preferred molecular structure being OH⟨⬡⟩— CH_2—⟨⬡⟩OH. This leads to the reduction in the polydispersity and gives

considerably lowered $\bar{M}_w$. For the values of R_3 studied for HCSTR, in figure 4.9, this is not found to occur even though the curves become close to each other for R_3 beyond 5.

In figure 4.10 and 4.11, the effect of $[P]_o / [F]_o$ on the mole fraction distribution of P_i and Q_i have been examined. In figure 4.10, the conversion of phenol (for x=0.20) is always found to be smaller and as a result of which the distribution curves appear steeper than those for batch reactors. Similarly in figure 4.11, $[Q_{1T}]$ $(= [Q_1] + [Q_1'])$ for HCSTR is larger. On calculation of the polydispersity index, $\mathcal{P}$, of the polymer found in HCSTR is always larger. In table 4.1 and 4.2 the effect of R_1 has been examined on the distributions of P_i and Q_i and results compared with those for batch reactors. Similar results are obtained when R_2 is varied and the MWD are found to be insensitive to these parameters.

TABLE 4.1

Effect of R1 on P_n; R2 = 0.30, R3 =2.40; X=0.90

R1		P_1	P_2	P_3	P_4	P_5	P_6	P_7	P_8	P_9
	Batch	0.2725	0.2012	0.1099	0.0583	0.0309	0.0163	0.0086	0.0045	0.0024
0.05	HCSTR	0.06233	0.1175	0.04597	0.02336	0.01341	0.00829	0.00538	0.0036	0.00249
	Batch	0.2741	0.2012	0.1092	0.0581	0.03087	0.01637	0.00868	0.0046	0.0024
0.15	HCSTR	0.6234	0.1175	0.04594	0.0234	0.0132	0.00832	0.00543	0.00365	0.00247
	Batch	0.2756	0.2013	0.1084	0.058	0.03082	0.01638	0.00871	0.0046	0.00246
0.25	HCSTR	0.6235	0.118	0.0461	0.024	0.0135	0.00836	0.00546	0.00366	0.0025
	Batch	0.2771	0.2014	0.1077	0.05765	0.03077	0.01639	0.00873	0.00455	0.00248
0.35	HCSTR	0.6239	0.1185	0.0462	0.0241	0.0136	0.00839	0.00548	0.00369	0.0025
	Batch	0.2793	0.2014	0.1066	0.0573	0.03069	0.01641	0.00877	0.00468	0.0025
0.50	HCSTR	0.6240	0.1187	0.0463	0.0244	0.01361	0.00840	0.00548	0.00369	0.00251
	Batch	0.2835	0.2016	0.1097	0.0566	0.03054	0.01642	0.00882	0.00479	0.00252
0.80	HCSTR	0.6241	0.1187	0.04632	0.6245	0.01363	0.00842	0.00548	0.00369	0.00252

Effect of R1 Q_n; R2 = 0.30, R3 = 2.4; X =0.9

	Q_1	Q_1'	Q_2	Q_3	Q_4	Q_5	Q_6	Q_7	Q_8
BATCH	0.01124	0.01656	0.01443	0.006978	0.003713	0.001962	0.001038	0.0005489	0.0002904
HCSTR	0.05215	0.006525	0.02772	0.01130	0.005898	0.003442	0.002148	0.001404	0.000948
BATCH	0.01099	0.01619	0.01406	0.006780	0.003619	0.001917	0.001017	0.0005393	0.0002859
HCSTR	0.05216	0.0065255	0.02773	0.011305	0.0058986	0.003448	0.0021485	0.0014048	0.000949
BATCH	0.01076	0.01583	0.01371	0.006593	0.003528	0.001874	0.0009962	0.0005296	0.0002816
HCSTR	0.5217	0.006526	0.027738	0.01131	0.005899	0.00345	0.002149	0.001405	0.00095
BATCH	0.01053	0.01549	0.01338	0.006415	0.003443	0.001833	0.0009766	0.0005204	0.0002773
HCSTR	0.52178	0.006527	0.02774	0.011318	0.005901	0.00346	0.002150	0.001406	0.000954
BATCH	0.01022	0.01500	0.01291	0.006166	0.003322	0.001774	0.0009486	0.0005071	0.0002711
HCSTR	0.52180	0.006531	0.0278	0.01132	0.005006	0.00352	0.002155	0.0014063	0.000955
BATCH	0.009648	0.01413	0.01206	0.005722	0.003104	0.001669	0.0008972	0.0004824	0.0002594
HCSTR	0.53186	0.006535	0.2784	0.01133	0.005907	0.00354	0.002164	0.001407	0.000958

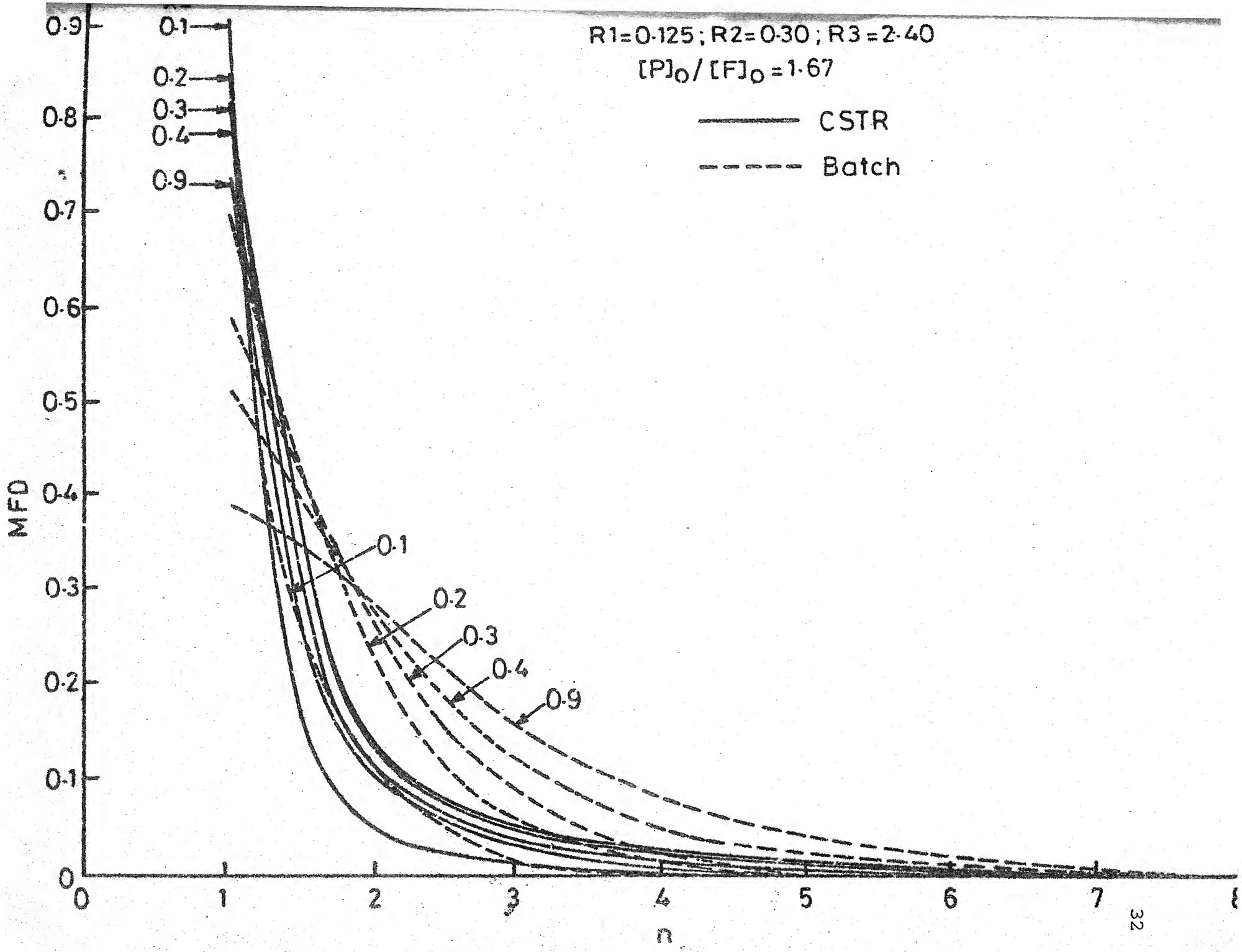
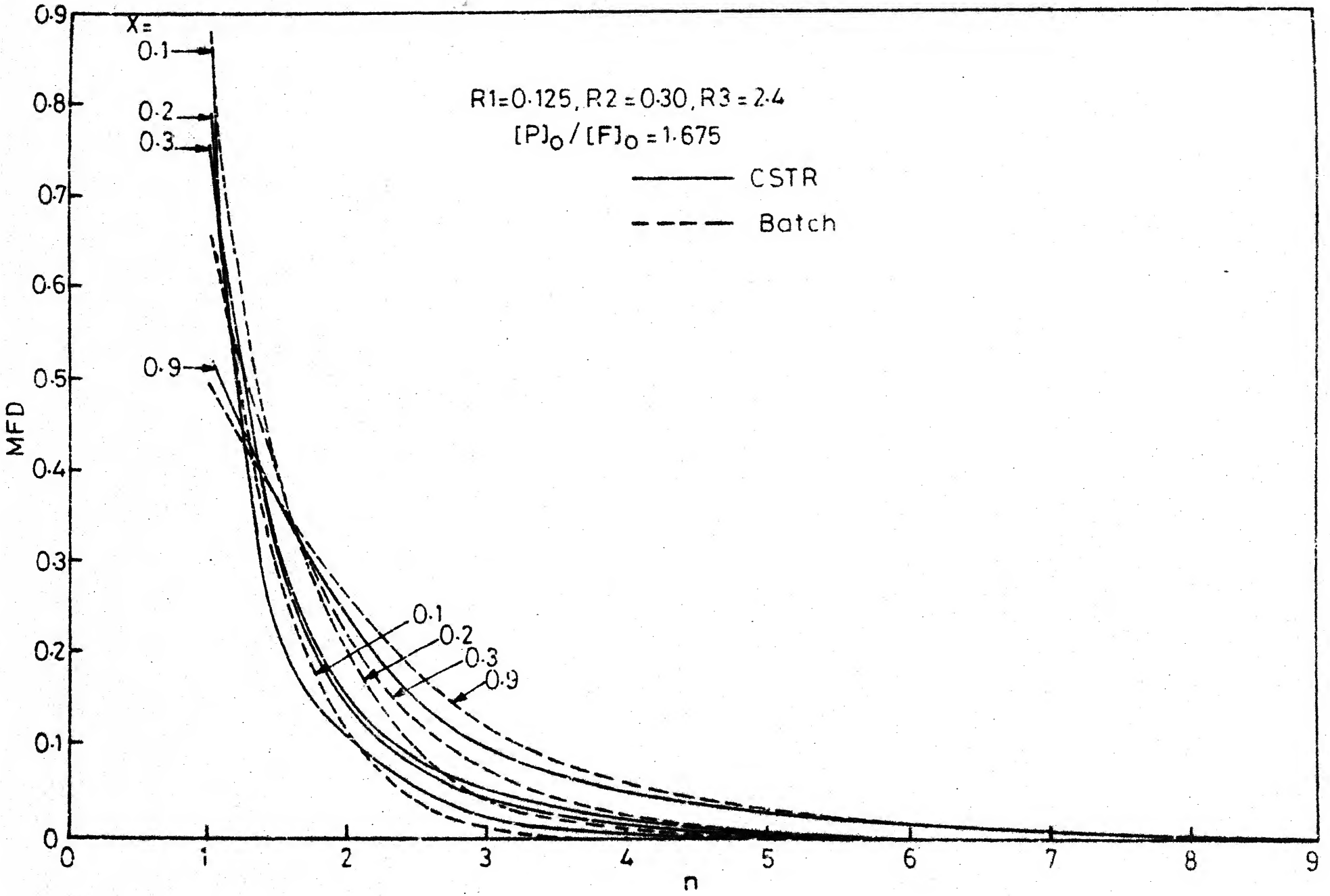


FIGURE 4.1 – Effect of Residence Time on MFD of P_i



FIGUR 4.2 - Effect of Residence Time on MFD of Q_i

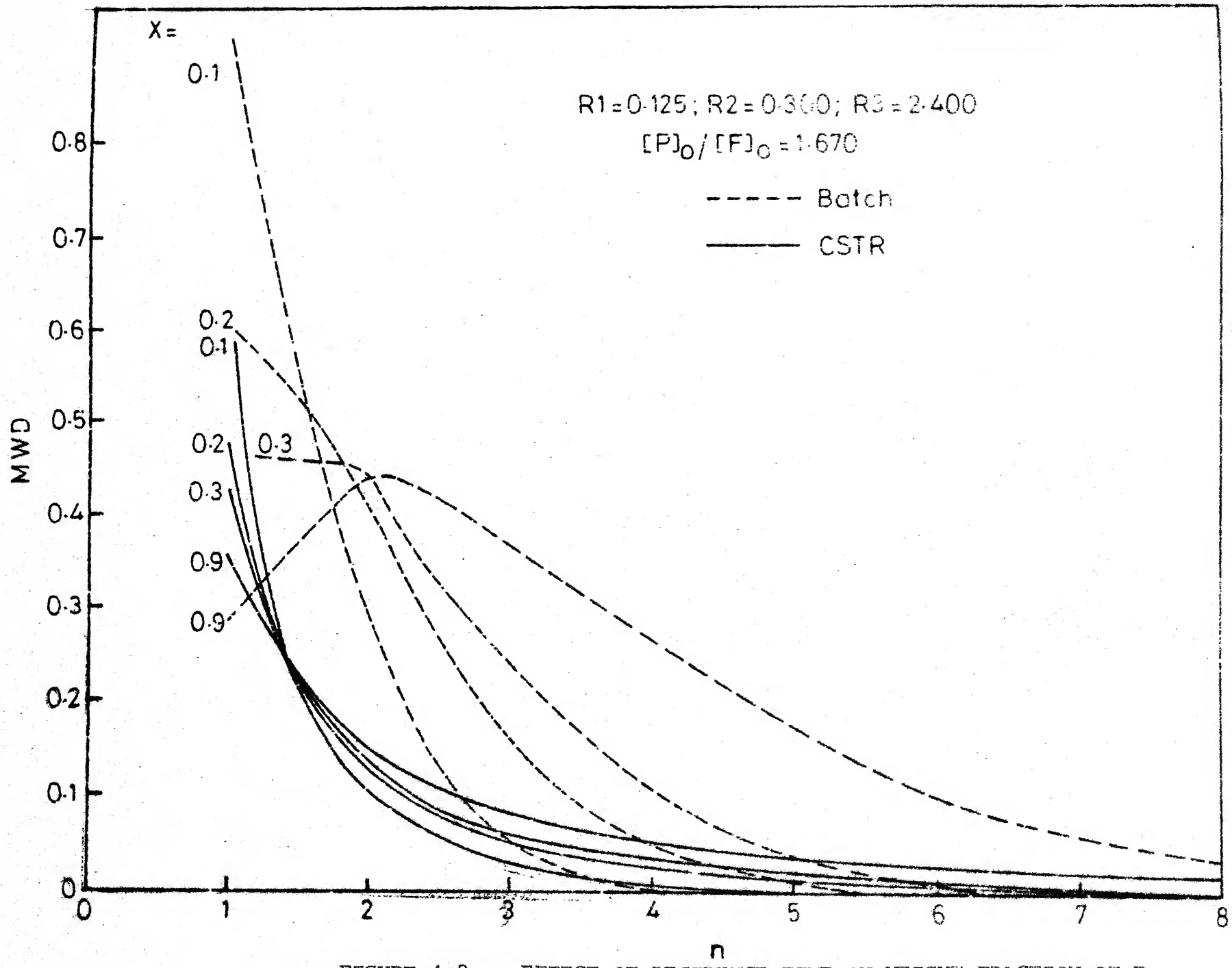


FIGURE 4.3 - EFFECT OF RESIDENCE TIME ON WEIGHT FRACTION OF P_i

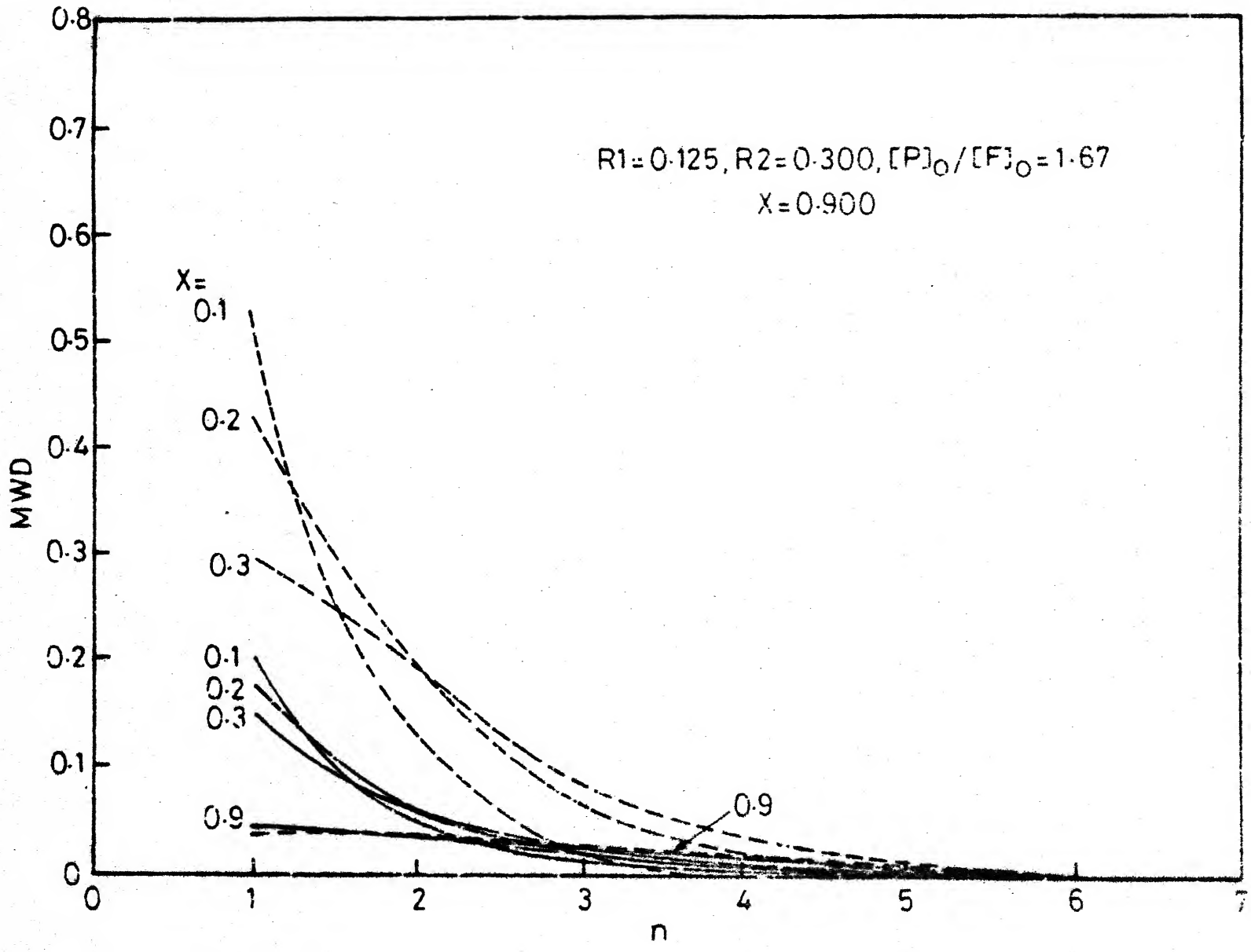


FIGURE 4.4 - Effect of Residence Time on Weight Fraction of Q_1

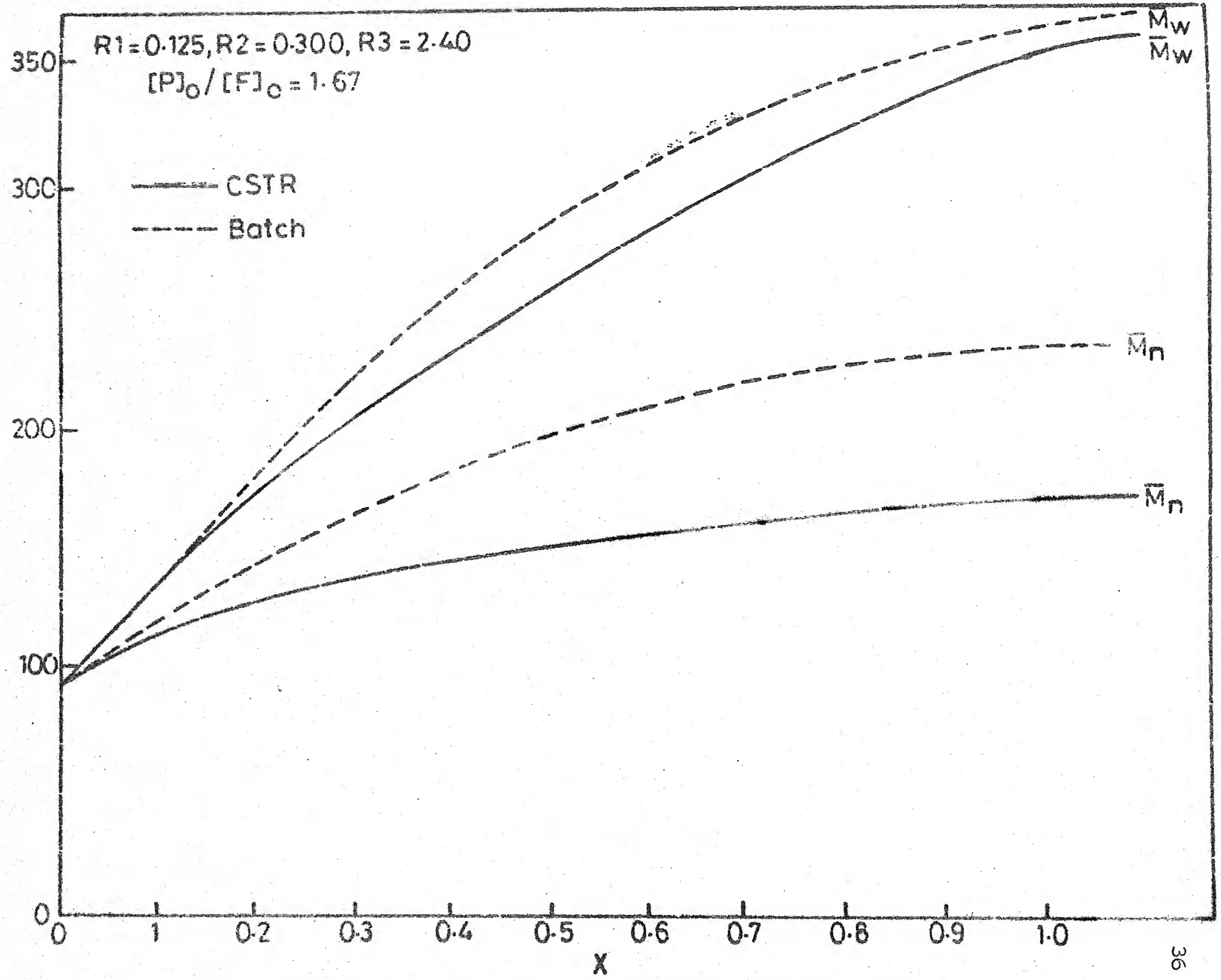


FIGURE 4.5 - $\bar{M}_n$, $\bar{M}_w$ Versus Dimensionless Time X

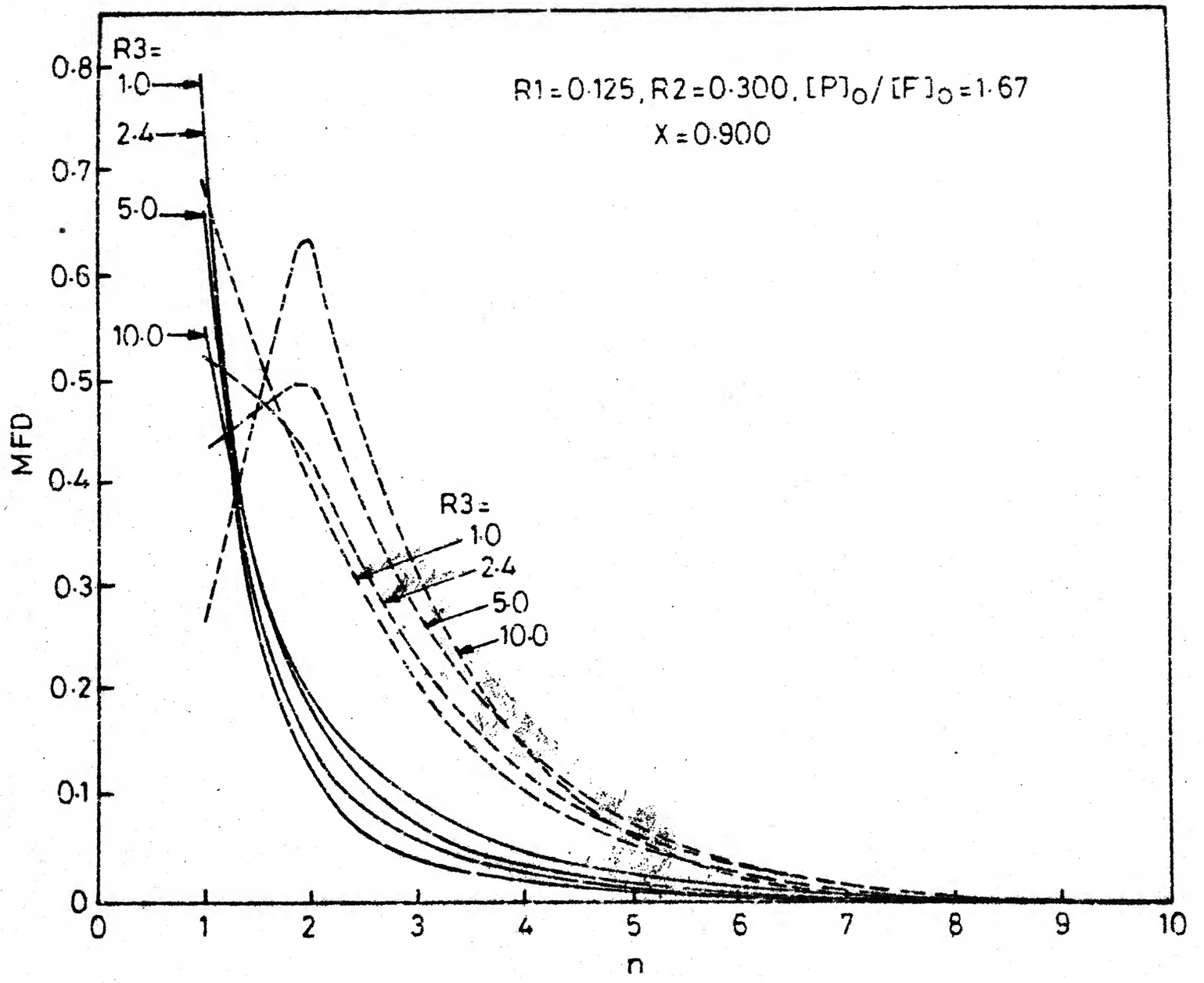


FIGURE 4.6 - Effect of R3 on the MFD of P_i

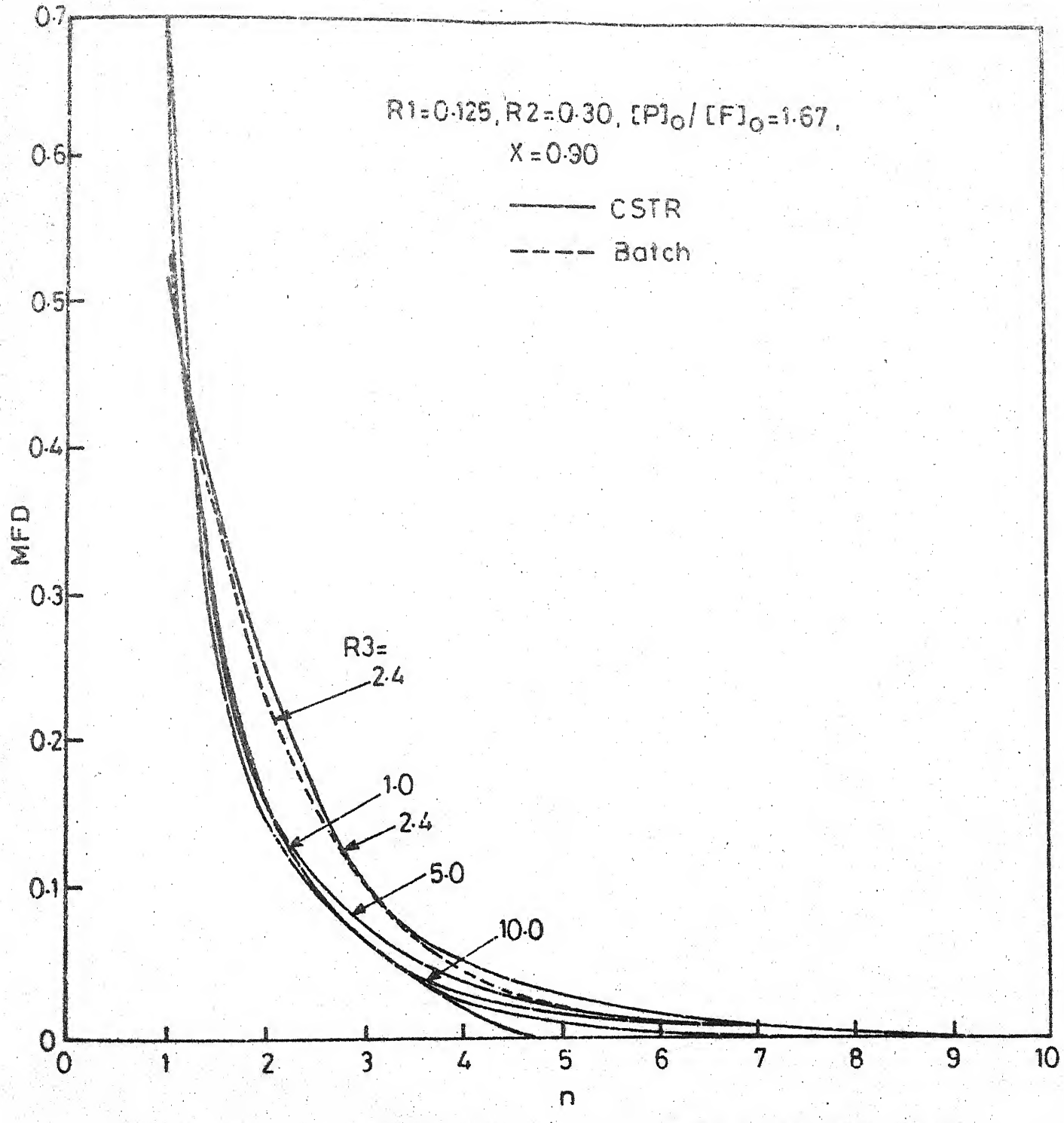


FIGURE 4.7 - Effect of R3 on the MFD of Q_1

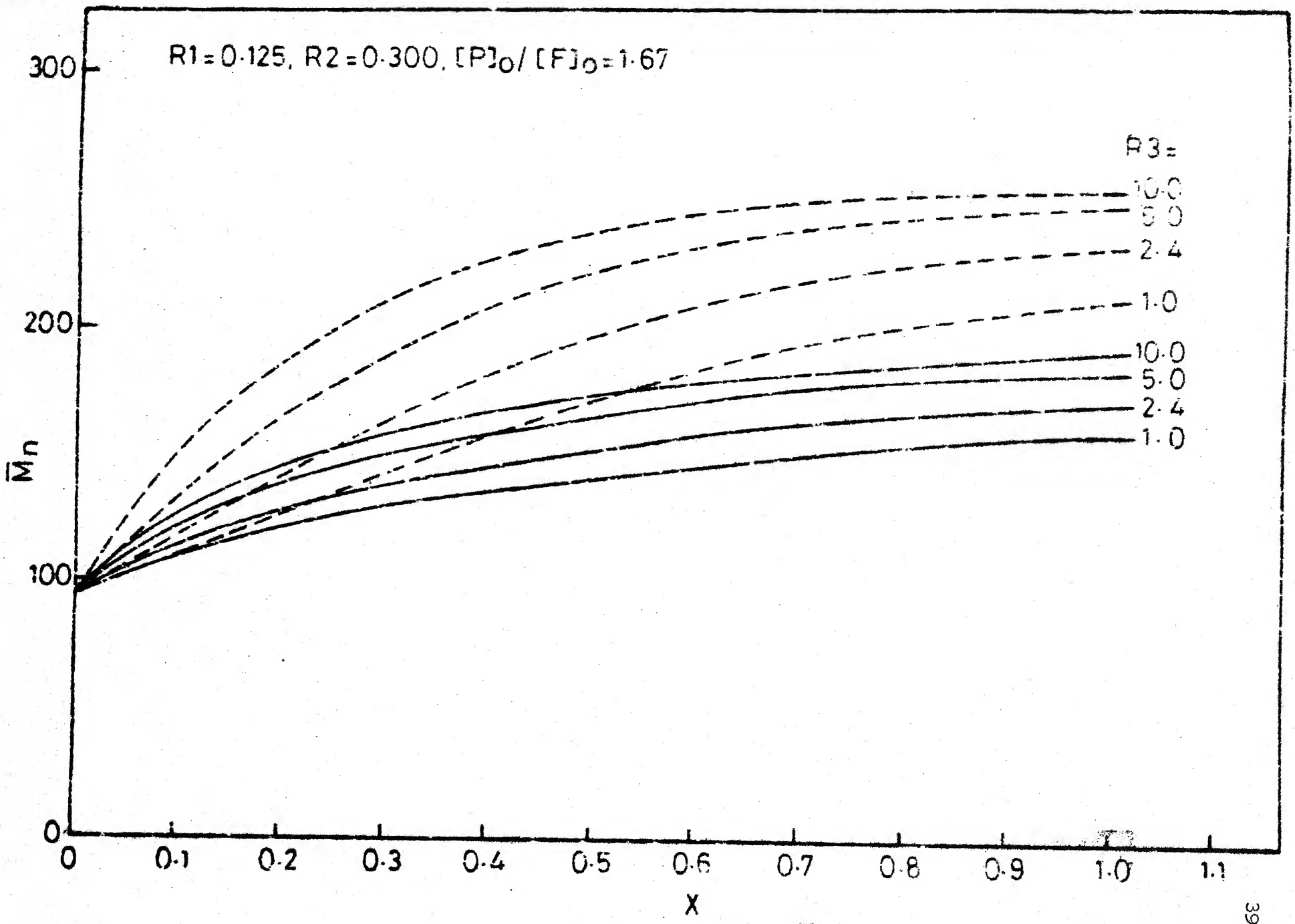


FIGURE 4.8 - Effect of R3 on $\bar{M}_n$

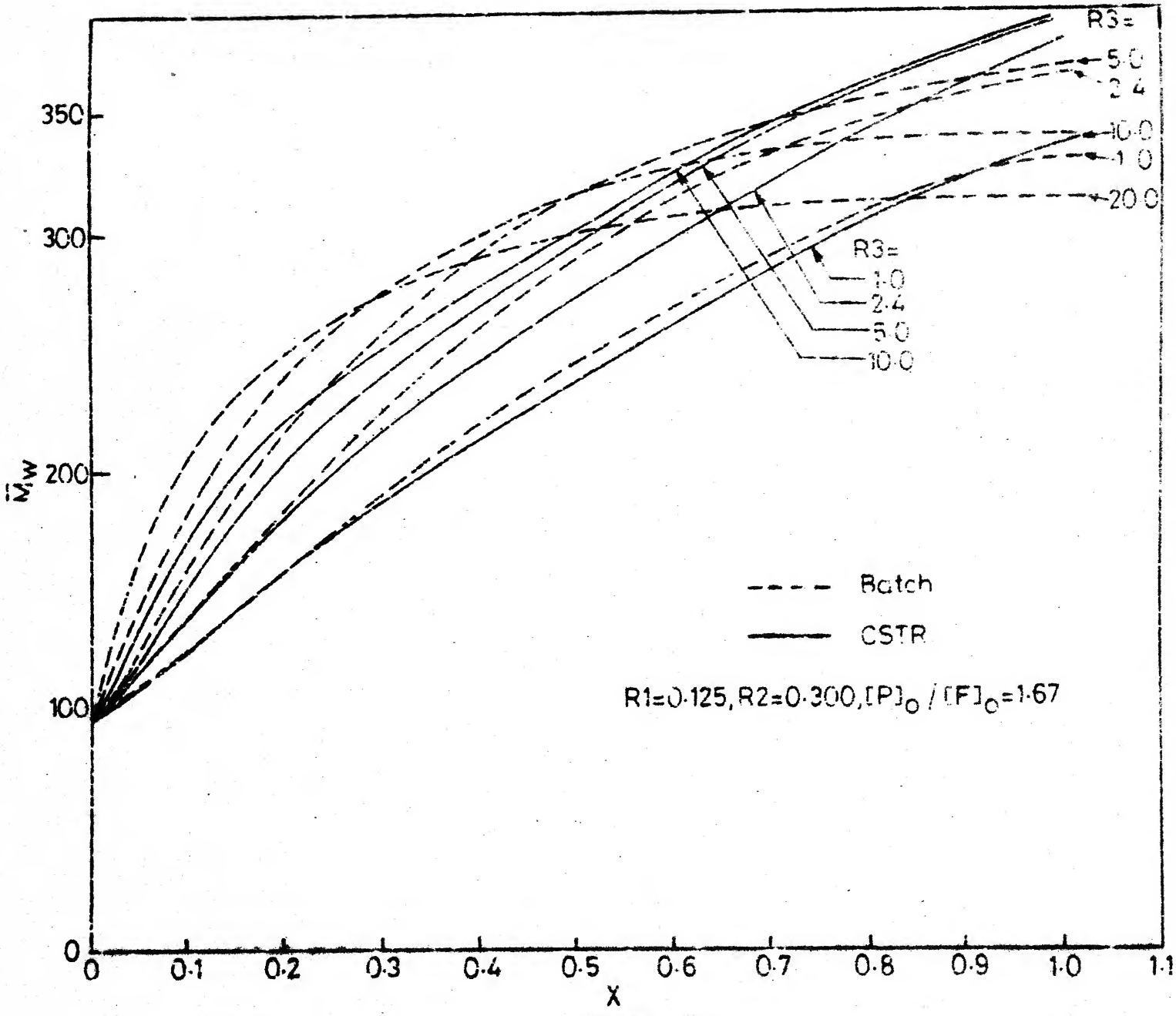


Fig.9

FIGURE 4.9 - Effect of R3 on $\bar{M}_w$

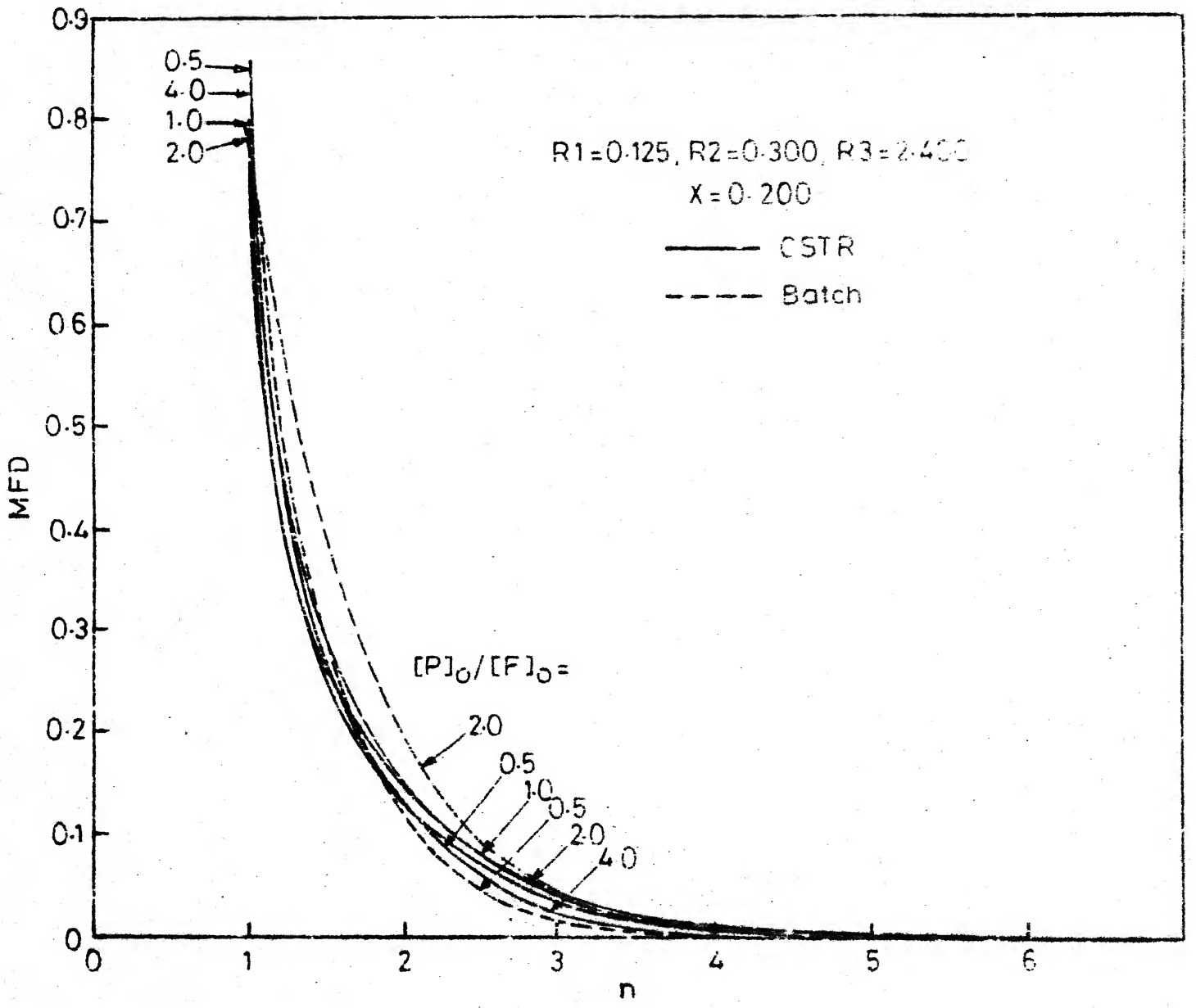


FIGURE 4.10 - Effect of P_o / F_o on the MFD of P_i

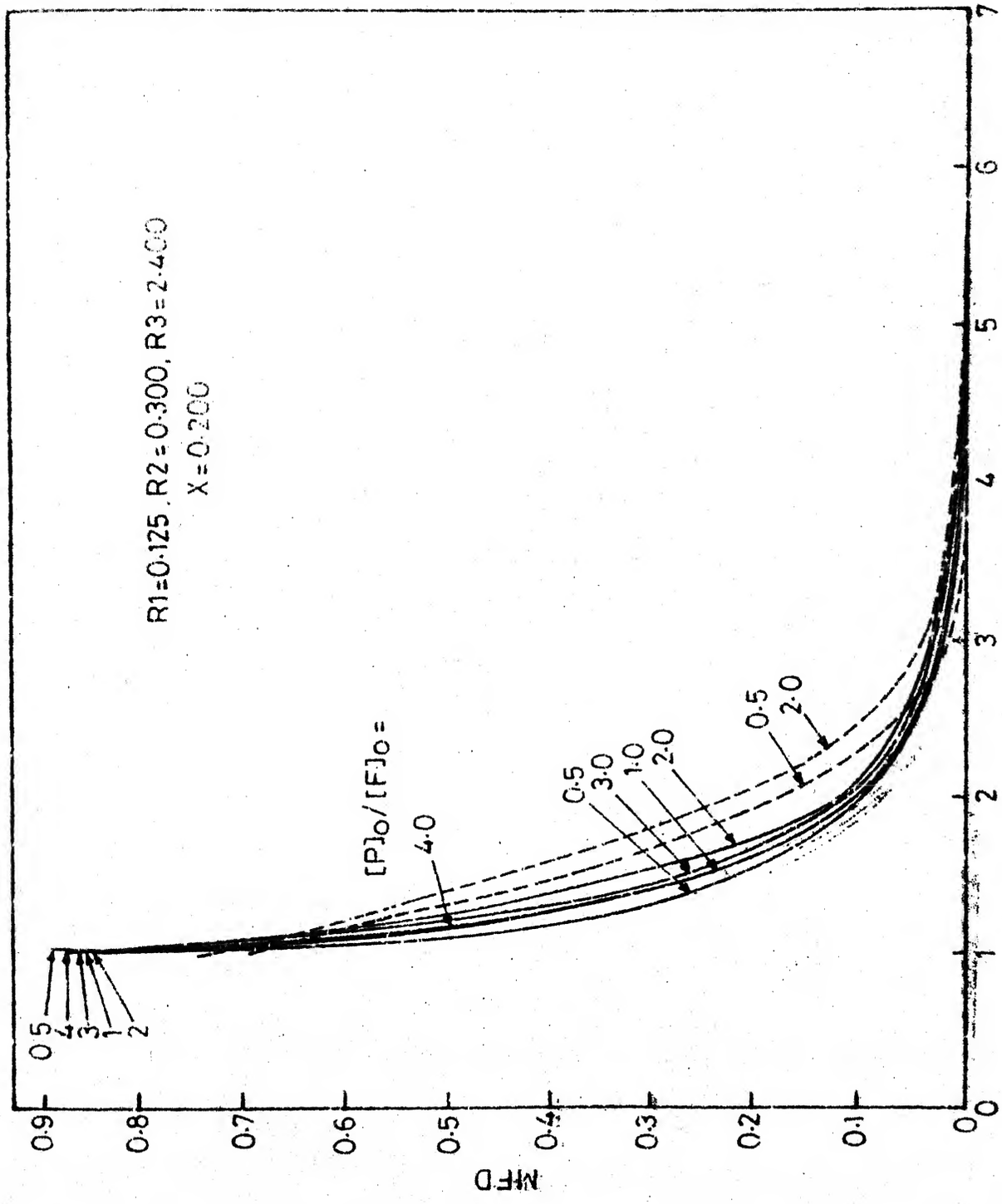


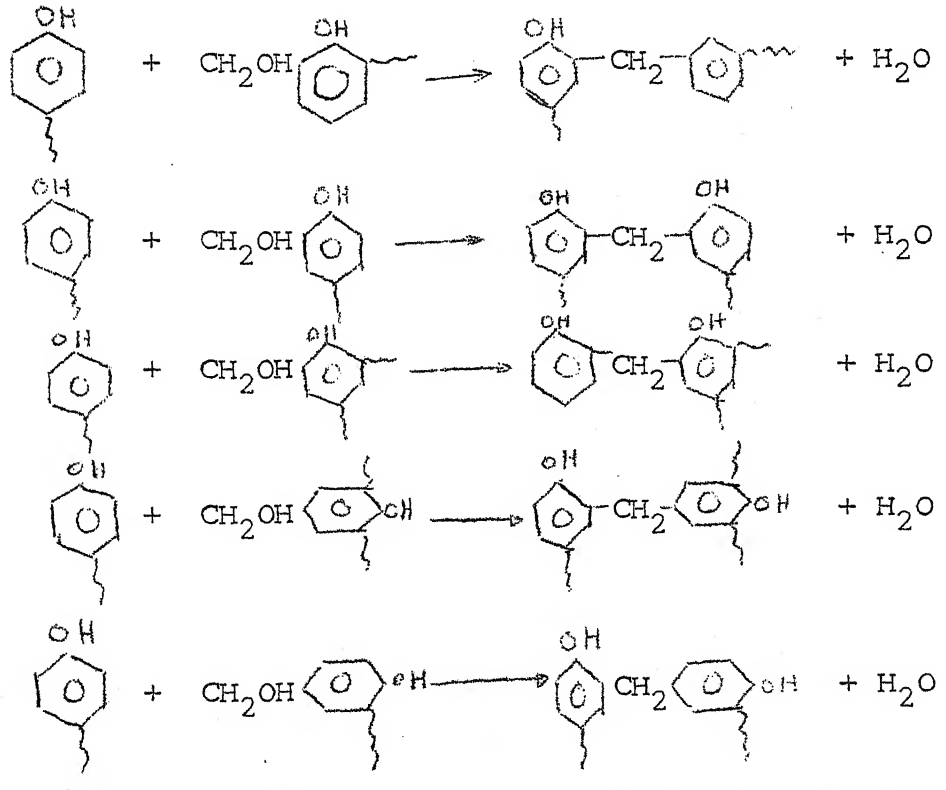
FIGURE 4.11 - Effect of P_o / F_o on the MFD Q_1

CHAPTER 5

MODEL WITH REVERSIBLE KINETICS

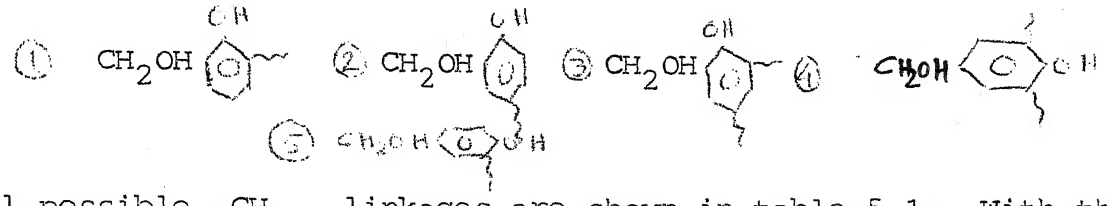
Earlier it was assumed that the condensation product water is removed continuously and hence reverse reactions donot take place. When this is not the case the kinetic model must be modified which is done as follows.

As an example one considers the case when a external O'_e site of any polymer molecule reacts with a bound $-CH_2OH$ group of another polymer molecule. This results in five different $-CH_2-$ linkages as shown below



To be able to write the mass balance taking the reverse reactions

into account it is necessary to distinguish the - CH_2 - linkages. Therefore the following - CH_2OH groups are distinguished.



All possible -CH_2 - linkages are shown in table 5.1. With these the forward reactions between different species are shown in table 5.2. In table 5.3 all reverse reactions are given. It is assumed that K_5 represents the rate constant involving - CH_2 - and H_2O.

A given bond can undergo several reactions for example 1,2 linkage reacts with a water molecule in the following two ways:

$$(1,2) + H_2O \longrightarrow (1) + 2O'_e - O_i$$

$$(1,2) + H_2O \longrightarrow (2) + O_e + P_e - P_i$$

Since it can react in two ways a rate constant of $K_5/2$ is assigned to each. This way the rate constant of each bond is decided. On the other hand when a - CH_2- linkage react with F, Q_1 or Q'_1, the nature of the bond gets changed. For example a 1,1 bond becomes 1,4 on reaction with F, Q_1 or Q'_1 or - CH_2OH. The forward reactions involving the interconversion are shown in table 5.4. The state of different sites are not shown in these reactions as it will lead to redundont counting. The reverse

reaction for interconversions of bonds are shown in table 5.5.

One is now in a position to write the mass balance equations for O_e', O_e, O_i, P_i, P_e, F, Q_1, Q_1', p and balance equations for all the linkages and five bound - CH_2OH, in the same way as done earlier.

To get the expression for MWD, the balance equations for all the species P_n and Q_n are written. Terms due to reverse reactions are added to each of the equations derived earlier for the irreversible case and the following equations results.

$$\frac{d[P_n]}{dt} = \frac{CN}{SUM}[P_{n-1}]\left([Q_1]+[Q_1']\right) + \sum_{i=2}^{n-3}\frac{CN}{SUM}[P_{n-1}][Q_i]$$

$$+ \frac{CM}{SUM}[P_2][Q_{n-2}] + (2K_1+K_4)[P][Q_{n-1}]$$

$$- \frac{2CN}{SUM}[P_n][F] - \frac{CN}{SUM}[P_n]\left(\sum_{2}[Q_m]+[Q_1]+[Q_1']\right)$$

$$-(n-1)K_5[P_n][H_2O] + K_5\sum_{i=n+1}[Q_i][H_2O] + 2K_5[H_2O]$$

$$\times \sum_{i=n+1}[P_i], n \geq 5 \qquad \text{(R-1)}$$

$$\frac{d[P_2]}{dt} = (2K_1+K_4)[P]\left([Q_1]+[Q_1']\right) - \frac{2CM}{SUM}[P_2][F]$$

$$- \frac{CM}{SUM}[P_2]\left(\sum_{m=2}[Q_m]+[Q_1]+[Q_1']\right) - K_5[P_2][H_2O]$$

$$+K_5\sum_{i=3}[Q_i][H_2O] + 2K_5[H_2O]\sum_{i=3}[P_i] + K_5[Q_2][H_2O] \qquad \text{(R-.)}$$

$$\frac{d[P_3]}{dt} = \frac{CM}{SUM}[P_2][Q_1] + \frac{CM}{SUM}[P_2][Q_1'] + (2K_1+K_4)[P][Q_2]$$

$$- \frac{2CN}{SUM}[P_3][F] - \frac{CN}{SUM}[P_3]\left(\sum_{m=2}[Q_m] + [Q_1] + [Q_1']\right)$$

$$-2K_5[P_3][H_2O] + K_5[H_2O]\sum_{i=4}[Q_i] + 2K_5[H_2O]\sum_{i=4}[P_i]$$

$$+ K_5[H_2O][Q_3] \qquad (R-3)$$

$$\frac{d[P_4]}{dt} = \frac{CN}{SUM}[P_3]([Q_1] + [Q_1']) + \frac{CM}{SUM}[P_2][Q_2]$$

$$(2K_1+K_4)[P][Q_3] - \frac{2CN}{SUM}[P_4][F]$$

$$- \frac{CN}{SUM}[P_4]\left(\sum_{n=2}[Q_m] + [Q_1] + [Q_1']\right) - 3K_5[H_2O][P_4]$$

$$+K_5[H_2O]\sum_{i=5}[Q_i] + 2K_5[H_2O]\sum_{i=5}[P_i] + K_5[Q_4][H_2O]$$

$$(R-4)$$

$$\frac{d\,Q_n}{dt} = -(2K_1+K_4)[Q_n][P] - \left\{CN.[Q_n] + \frac{CN}{SUM}[Q_n]\left(\sum_{m=2}[Q_m]\right.\right.$$

$$\left.\left. + [Q_1] + [Q_1']\right) + [Q_n](2K_1[Q_1'] + K_1[Q_1] + K_4[Q_1])\right\}$$

$$+ \frac{2CN}{SUM}[P_n][F] + \frac{CN}{SUM}\sum_{i=1}^{n-3}[Q_i][Q_{n-i}] + \frac{CM}{SUM}[Q_2][Q_{n-2}$$

$$\frac{CM}{SUM}[Q_1][Q_{n-1}]+(K_1+K_4)[Q_1][Q_{n-1}] + \frac{CN}{SUM}[Q_{n-1}][Q_1'] + 2K_1[Q_1'][Q_{n-1}]$$

$$- K_5[Q_n][H_2O] - K_5[Q_n](n-1)[H_2O] + K_5 \sum_{i=n+1} [Q_i] H_2O$$

$$n \geq 4 \qquad \text{(R-5)}$$

$$\frac{d[Q_3]}{dt} = -(2K_1+K_4)[Q_3][P] - CN[Q_3] - \frac{CN}{SUM}[Q_3]\left(\sum_2 [Q_m] + [Q_1] + [Q_1']\right) - [Q_3](2K_1[Q_1'] + K_1[Q_1] + K_4[Q_1])$$

$$+ \frac{"2CN}{SUM}[P_3][F] + (K_1+K_4)[Q_1][Q_2] + 2K_1[Q_1'][Q_2]$$

$$+ \frac{CM}{SUM}[Q_2]([Q_1] + [Q_1']) - K_5[Q_3][H_2O] - 2K_5[Q_3]$$

$$\times[H_2O] + K_5 \sum_4 [Q_i][H_2O] \qquad \text{(R-6)}$$

$$\frac{d[Q_2]}{dt} = (K_1+K_4)[Q_1]^2 + (3K_1+K_4)[Q_1][Q_1'] + 2K_1[Q_1']^2$$

$$+ \frac{2CM}{SUM}[P_2][F] - (2K_1+K_4)[Q_2][P] - CN[Q_2]$$

$$- \frac{CM}{SUM}[Q_2]\left(\sum_{m=2}[Q_m] + [Q_1] + [Q_1']\right)$$

$$- [Q_2](2K_1[Q_1'] + K_1[Q_1] + K_4[Q_1]) - K_5[Q_2][H_2O]$$

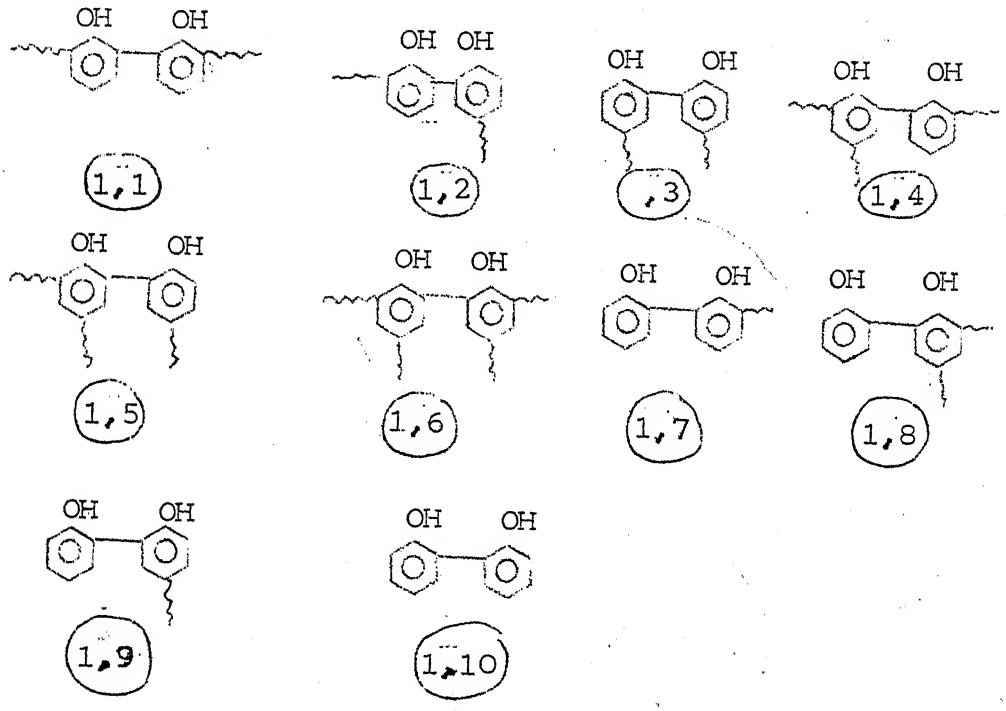
$$- K_5[Q_2][H_2O] + K_5 \sum_{i=3} [Q_i][H_2O] \qquad \text{(R-7)}$$

Equation R-1 is the rate expression for P_n, $n \geq 5$. The reverse reaction in which P_n disintegrates contributes the term $(n-1)\, K_5 [P_n] [H_2O]$ for there are (n-1) bonds in P_n. P_n can be produced if any Q_i ($i \geq n+1$) is attacked by a water molecule. Ther term $K_5 \sum_{i=n+1} [Q_i] [H_2O]$ is thus accounted for. On the other hand P_n is also produced when a P_i ($i \geq n+1$) reacts with water. It can be noted that the breaking of bond from either side of P_i ($i \geq n+1$) will lead to formation of P_n and this leads to the term $2K_5 [H_2O] \sum_{i=n+1} [P_i]$. In similar ways, the equations for other species are written.

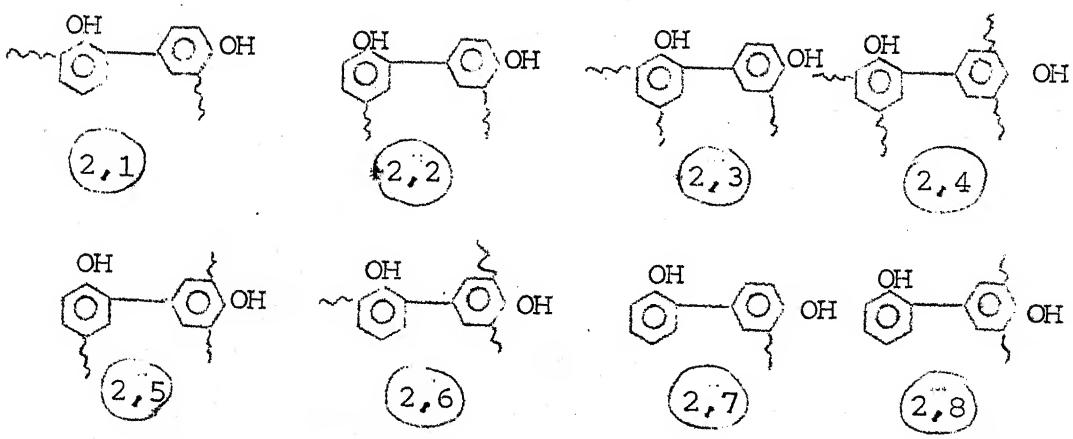
TABLE 5.1

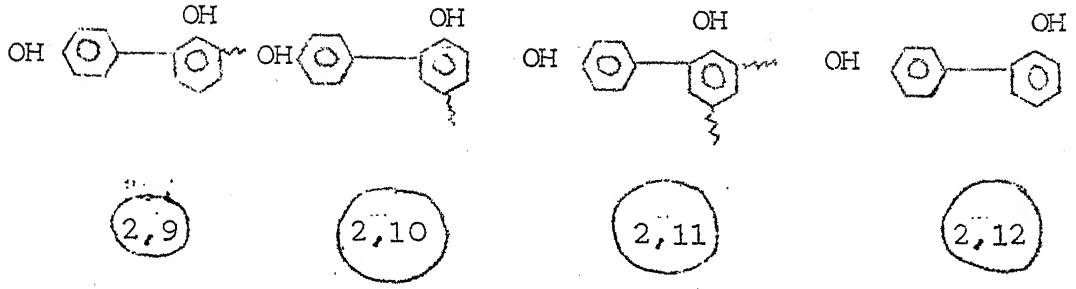
Different Types of $-CH_2-$ Linkages

(a) O–O linkages

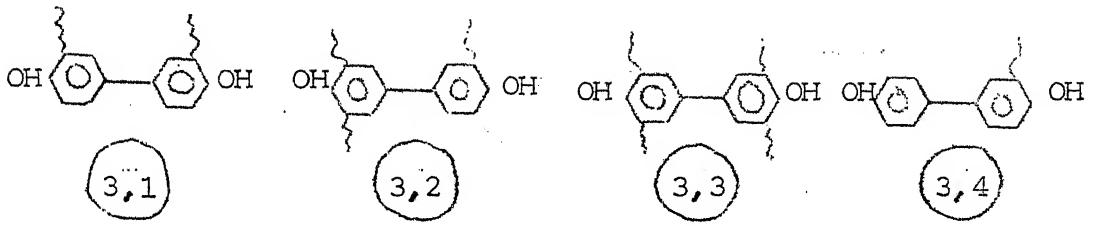


(b) O–p linkages





(c) p–p Linkages



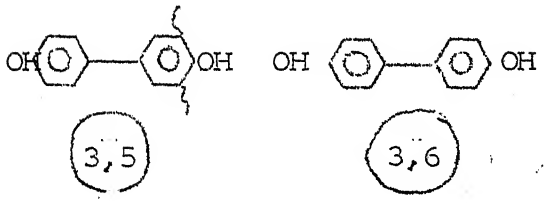


TABLE 5.2

FORWARD REACTIONS

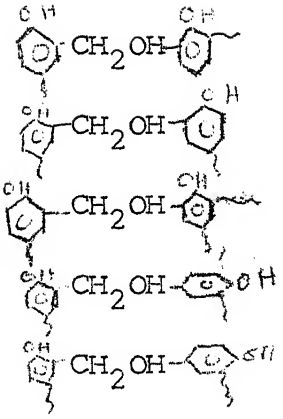
We are not calling a CH_2OH as a bond.

(a) Reactions with F

1. $O_e' + F \xrightarrow{4K_1} (2) - O_e' + O_i + H_2O$
2. $O_e + F \xrightarrow{K_1} (1) - P_e + P_i + H_2O$
3. $O_i + F \xrightarrow{K_2} (3) + H_2O$
4. $P_i + F \xrightarrow{K_3} (4) + H_2O$
5. $P_e + F \xrightarrow{K_4} (5) + O_i - O_e + H_2O$

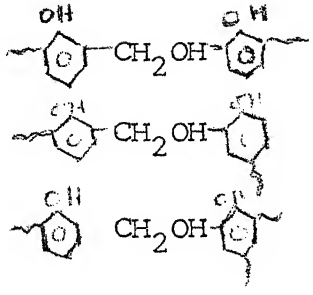
(b) O_e' with CH_2OH

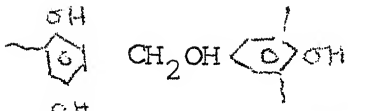
1. $O_e' + (1) \xrightarrow{2K_1} (1,2) + O_i - O_e' + H_2O$
2. $O_e' + (2) \xrightarrow{2K_1} (1,3) + O_i - O_e' + H_2O$
3. $O_e' + (3) \xrightarrow{2K_1} (1,5) + O_i - O_e' + H_2O$
4. $O_e' + (4) \xrightarrow{2K_1} (2,5) + O_i - O_e' + H_2O$
5. $O_e' + (5) \xrightarrow{2K_1} (2,2) + O_i - O_e' + H_2O$

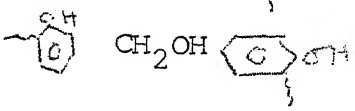


(c) O_e with CH_2OH

1. $O_e + (1) \xrightarrow{K_1} (1,1) + P_i - P_e + H_2O$
2. $O_e + (2) \xrightarrow{K_1} (1,2) + P_i - P_e + H_2O$
3. $O_e + (3) \xrightarrow{K_1} (1,4) + P_i - P_e + H_2O$



4. O_e + (4) $\xrightarrow{K_1}$ (2,6) $+p_i-p_e+H_2O$ 

5. O_e + (5) $\xrightarrow{K_1}$ (2,1) + $p_i-p_e+H_2O$ 

(d) O_i with CH_2OH

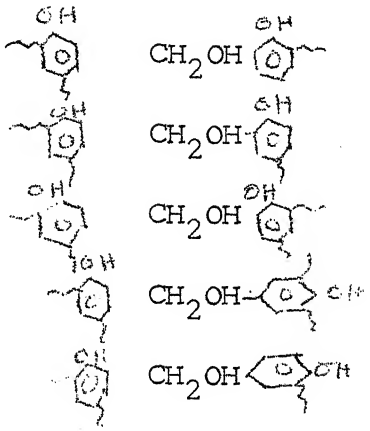
1. O_i + (1) $\xrightarrow{K_2}$ (1,4) + H_2O

2. O_i + (2) $\xrightarrow{K_2}$ (1,5) + H_2O

3. O_i + (3) $\xrightarrow{K_2}$ (1,6) + H_2O

4. O_i + (4) $\xrightarrow{K_2}$ (2,4) + H_2O

5. O_i + (5) $\xrightarrow{K_2}$ (2,3) + H_2O



(e) P_i with CH_2OH

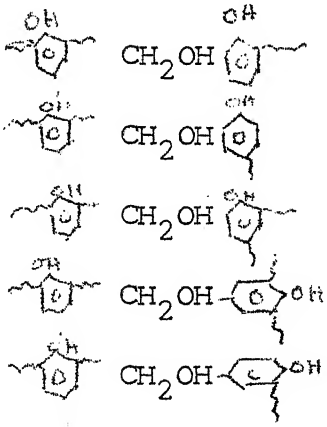
1. p_i + (1) $\xrightarrow{K_3}$ (2,6) + H_2O

2. p_i + (2) $\xrightarrow{K_3}$ (2,5) + H_2O

3. p_i + (3) $\xrightarrow{K_3}$ (2,4) + H_2O

4. p_i + (4) $\xrightarrow{K_3}$ (3,3) + H_2O

5. p_i + (5) $\xrightarrow{K_3}$ (3,2) + H_2O



(f) P_e with CH_2OH

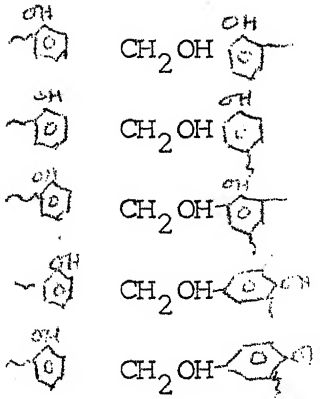
1. p_e + (1) $\xrightarrow{K_4}$ (2,1) + $O_i-O_e+H_2O$

2. p_e + (2) $\xrightarrow{K_4}$ (2,2) + $O_i-O_e+H_2O$

3. p_e + (3) $\xrightarrow{K_4}$ (2,3) + $O_i-O_e+H_2O$

4. p_e + (4) $\xrightarrow{K_4}$ (3,2) + $O_i-O_e+H_2O$

5. p_e + (5) $\xrightarrow{K_4}$ (3,1) + $O_i-O_e+H_2O$



(g) Rxn of P with F and CH_2OH

1. $P + F \xrightarrow{4K_1} Q_1 + H_2O$

   $P + F \xrightarrow{2K_4} Q_1' + H_2O$

2. $P + (1) \xrightarrow{2K_1} (1,7) + O_e + p_e + H_2O$

3. $P + (2) \xrightarrow{2K_1} (1,9) + O_e + p_e + H_2O$

4. $P + (3) \xrightarrow{2K_1} (1,8) + O_e + p_e + H_2O$

5. $P + (4) \xrightarrow{2K_1} (2,8) + O_e + p_e + H_2O$

6. $P + (5) \xrightarrow{2K_1} (2,7) + O_e + p_e + H_2O$

7. $P + (1) \xrightarrow{K_4} (2,9) + 2O_e' + H_2O$

8. $P + (2) \xrightarrow{K_4} (2,10) + 2O_e' + H_2O$

9. $P + (3) \xrightarrow{K_4} (2,11) + 2O_e' + H_2O$

10. $P + (4) \xrightarrow{K_4} (3,5) + 2O_e' + H_2O$

11. $P + (5) \xrightarrow{K_4} (3,4) + 2O_e' + H_2O$

(h) Rxns of P with Q_1 and Q_1'

1. $P + Q_1' \xrightarrow{2K_1} P_e + 2O_e' + O_e + H_2O + (2,12)$

2. $P + Q_1' \xrightarrow{K_4} (3,6) + 4O_e' + H_2O$

3. $P + Q_1 \xrightarrow{2K_1} (1,10) + 2p_e + 2O_e + H_2O$

4. $P + Q_1 \xrightarrow{K_4} (2,12) + O_e + p_e + 2O_e' + H_2O$

(i) Rxns of Q_1 and Q_1' with sites

1. $O_e' + Q_1' \xrightarrow{K_1} O_i + 2O_e' - O_e' + (2,10) + H_2O$

2. $O_e' + Q_1 \xrightarrow{K_1} 1,9 + p_e + O_e + O_i - O_e' + H_2O$

3. $O_e + Q_1' \xrightarrow{K_1} 2,9 + 2O_e' + p_i - p_e + H_2O$

4. $O_e + Q_1 \xrightarrow{K_1} (1,7) + O_e + p_e + p_i + H_2O - p_e$

5. $p_i + Q_1' \xrightarrow{K_3} (2O_e') + 3,5 + H_2O$

6. $p_i + Q_1 \xrightarrow{K_3} (2,8) + O_e + p_e + H_2O$

7. $O_i + Q_1' \xrightarrow{K_2} (2,11) + 2O_e' + H_2O$

8. $O_i + Q_1 \xrightarrow{K_2} (1,8) + O_e + p_e + H_2O$

9. $p_e + Q_1' \xrightarrow{K_4} (3,4) + O_i - O_e + 2O_e' + H_2O$

10. $p_e + Q_1 \xrightarrow{K_4} (2,7) + O_e + p_e + O_i - O_e + H_2O$

(j) Rxns of Q_1 and Q_1' with CH_2OH

1. $Q_1 + (1) \xrightarrow{K_3} (2,7) + Q_e + p_e - p_i + (3)$

$\xrightarrow{K_1} (1,1) + (1) + p_i$

$\xrightarrow{K_4} (2,1) + (2) + O_i$

2. $Q_1 + 2 \xrightarrow{K_2} (1,8) + H_2O - O_i + (3) + O_e + p_e$

$\xrightarrow{K_1} (1,2) + H_2O + p_i + (1)$

$\xrightarrow{K_4} (2,2) + H_2O + O_i + (2)$

3. $Q_1 + 3 \xrightarrow{K_4} (1,5) + H_2O + p_i + (1)$

$\xrightarrow{K_4} (2,3) + H_2O + O_i + (2)$

4. $Q_1 + (4) \xrightarrow{K_1} (2,6) + H_2O + p_i + (1)$

$\xrightarrow{K_4} (3,2) + H_2O + o_i + (2)$

5. $Q_1 + (5) \xrightarrow{K_2} (1,8) + H_2O - o_i + (4) + o_e + p_e$

$\xrightarrow{K_1} (2,1) + H_2O + p_i + (1)$

$\xrightarrow{K_4} (3,1) + H_2O + o_i + (2)$

6. $Q_1' + (1) \xrightarrow{2K_1} (1,2) + H_2O + o_i + (5)$

$\xrightarrow{K_3} (3,5) + H_2O + 2o_e' - p_i + (3)$

7. $Q_1' + (2) \xrightarrow{2K_1} (1,3) + H_2O + o_i + (5)$

$\xrightarrow{K_2} (2,11) + H_2O - o_i + 2o_e' + (3)$

8. $Q_1' + (3) \xrightarrow{2K_1} (1,5) + H_2O + o_i + (5)$

9. $Q_1' + (4) \xrightarrow{2K_1} (2,5) + H_2O + o_i + (5)$

10. $Q_1' + (5) \xrightarrow{2K_1} (2,2) + H_2O + o_i + (5)$

$\xrightarrow{K_2} (2,11) + H_2O - o_i + 2o_e' + (4)$

11. $Q_1 + Q_1' \xrightarrow{2K_1} (1,9) + H_2O + o_e + p_e + o_i + (5)$

$\xrightarrow{K_1} (2,9) + H_2O + 2o_e' + p_i + (1)$

$\xrightarrow{K_4} (3,4) + H_2O + 2o_e' + o_i + (2)$

12. $Q_1 + Q_1 \xrightarrow{2K_1} (1,7) + H_2O + o_e + p_e + p_i + (1)$

$\xrightarrow{2K_4} (2,7) + H_2O + o_e + p_e + o_i + (2)$

13. $Q_1' + Q_1' \xrightarrow{4K_1} (2,10) + 2o_e' + o_i + 5$

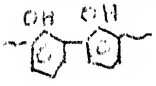
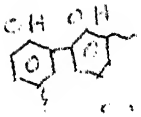
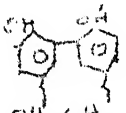
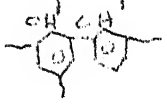
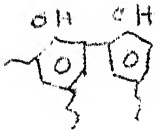
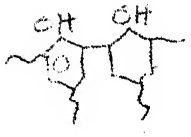
TABLE 5.3

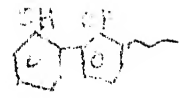
REVERSE REACTIONS

(a) With $-CH_2OH$

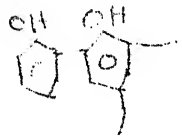
1. (1) + H_2O —K_5— $F + O_e + p_e - p_i$
2. (2) + H_2O —K_5— $2O'_e + F - O_i$
3. (3) + H_2O —K_5— $O_i + F$
4. (4) + H_2O —K_5— $p_i + F$
5. (5) + H_2O —K_5— $O_e + p_e - O_i + F$

(b) With $-CH_2-$ Linkages

1.  (1,1) + H_2O —K_5— (1) + $O_e + p_e - p_i$
2.  (1,2) + H_2O —$\frac{1}{2}K_5$— (1) + $2O'_e - O_i$
   —$\frac{1}{2}K_5$— (2) + $O_e + p_e - p_i$
3.  (1,3) + H_2O —K_5— (2) + $2O'_e - O_i$
4.  (1,4) + H_2O —$\frac{1}{2}K_5$— (1) + O_i
   —$\frac{1}{2}K_5$— (3) + $O_e + p_e - p_i$
5.  (1,5) + H_2O —$\frac{1}{2}K_5$— (2) + O_i
   —$\frac{1}{2}K_5$— (3) + $2O'_e - O_i$
6.  (1,6) + H_2O —K_5— (3) + O_i

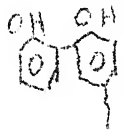
7. 

$(1,7) + H_2O \xrightarrow{\frac{1}{2}K_5} Q_1 - O_e - P_e + O_e + P_e - P_i$

8. 

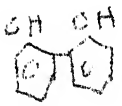
$(1,8) + H_2O \xrightarrow{\frac{1}{2}K_5} P - O_e - P_e + (1)$

$\xrightarrow{\frac{1}{2}K_5} Q_1 - O_e - P_e + O_i$

9. 

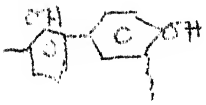
$(1,9) + H_2O \xrightarrow{\frac{1}{2}K_5} (3) - O_e - P_e + P$

$\xrightarrow{\frac{1}{2}K_5} Q_1 - O_e - P_e + 2O_e - O_i$

10. 

$(1,10) + H_2O \xrightarrow{\frac{1}{2}K_5} P + (2) - O_e - P_e$

$\xrightarrow{K_5} 2Q_1 - 2O_e - 2P_e$

11. 

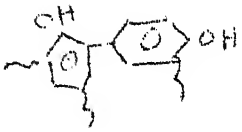
$(2,1) + H_2O \xrightarrow{\frac{1}{2}K_5} (1) + O_e + P_e - O_i$

$\xrightarrow{\frac{1}{2}K_5} (5) + O_e + P_e - P_i$

12. 

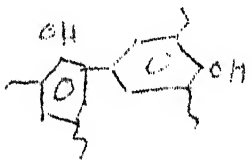
$(2,2) + H_2O \xrightarrow{\frac{1}{2}K_5} (2) + O_e + P_e - O_i$

$\xrightarrow{\frac{1}{2}K_5} (5) + 2O_e' - O_i$

13. 

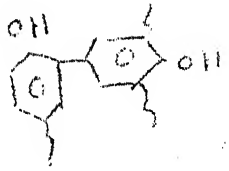
$(2,3) + H_2O \xrightarrow{\frac{1}{2}K_5} (3) + O_e + P_e - O_i$

$\xrightarrow{\frac{1}{2}K_5} (5) + O_i$

14. 

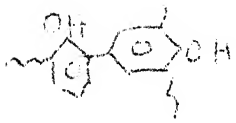
$(2,4) + H_2O \xrightarrow{\frac{1}{2}K_5} (4) + O_i$

$\xrightarrow{\frac{1}{2}K_5} (3) + P_i$

15. 

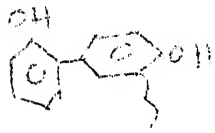
$(2,5) + H_2O \xrightarrow{\frac{1}{2}K_5} (4) + 2O_e' - O_i$

$\xrightarrow{\frac{1}{2}K_5} (2) + P_i$

16. 

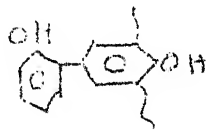
(2,6) + H_2O $\xrightarrow{\frac{1}{2}K_5}$ (1) + p_i

$\xrightarrow{\frac{1}{2}K_5}$ (4) + $O_e + p_e - p_i$

17. 

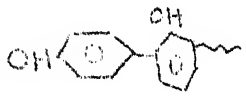
(2,7) + H_2O $\xrightarrow{\frac{1}{2}K_5}$ $Q_1 - O_e - p_e + O_e + p_e - O_i$

$\xrightarrow{\frac{1}{2}K_5}$ $P - O_e - p_e +$ (5)

18. 

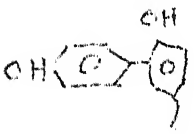
(2,8) + H_2O $\xrightarrow{\frac{1}{2}K_5}$ (4) + $P - O_e - p_e$

$\xrightarrow{\frac{1}{2}K_5}$ $Q_1 - O_e - p_e + p_i$

19. 

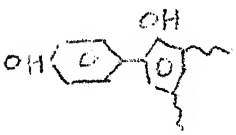
(2,9) + H_2O $\xrightarrow{\frac{1}{2}K_5}$ $Q_1' + O_e + p_e - p_i - 2O_e'$

$\longrightarrow$ $P +$ (1) $- 2O_e'$

20 

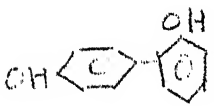
(2,10) + H_2O $\xrightarrow{\frac{1}{2}K_5}$ (2) + $P - 2O_e'$

$\xrightarrow{\frac{1}{2}K_5}$ $Q_1' + 2O_e' - O_i - 2O_e'$

21. 

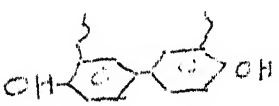
(2,11) + H_2O $\xrightarrow{\frac{1}{2}K_5}$ $Q_1' - 2O_e' + O_i$

$\xrightarrow{\frac{1}{2}K_5}$ $P - 2O_e' +$ (3)

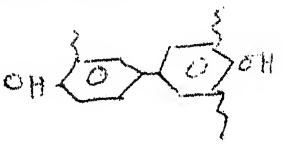
22. 

(2,12) + H_2O $\xrightarrow{\frac{1}{2}K_5}$ $Q_1' - 2O_e' - O_e - p_e + P$

$\xrightarrow{\frac{1}{2}K_5}$ $Q_1 - 2O_e' - O_e - p_e + P$

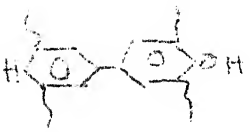
23. 

(3,1) + H_2O $\xrightarrow{K_5}$ (5) + $O_e + p_e - O_i$

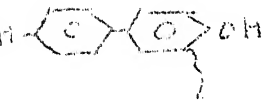
24. 

(3,2) + H_2O $\xrightarrow{\frac{1}{2}K_5}$ (4) + $O_e + p_e - O_i$

$\xrightarrow{\frac{1}{2}K_5}$ (5) + p_i

25. 

$$(3,3) + H_2O \xrightarrow{K_5} (4) + p_i$$

26. 

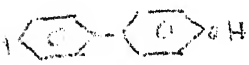
$$(3,4) + H_2O \xrightarrow{\frac{1}{2}K_5} Q_1' - 2O_e' + O_e + p_e - O_i$$

$$\xrightarrow{\frac{1}{2}K_5} P - 2O_e' + (5)$$

27. 

$$(3,5) + H_2O \xrightarrow{\frac{1}{2}K_5} Q_1' - 2O_e' + p_i$$

$$\xrightarrow{\frac{1}{2}K_5} P - 2O_e' + (4)$$

28. 

$$(3,6) + H_2O \xrightarrow{K_5} 2Q_1' - 4O_e'$$

TABLE 5.4

Interconversions of Bonds

CX Stands for sum of $-CH_2OH, F, Q_1, Q_1'$

1. (1,1) + CX $\xrightarrow{2K_3}$ (1,4) + H_2O
2. (1,2) + CX $\xrightarrow{K_2}$ (1,4) + H_2O
   $\xrightarrow{K_3}$ (1,5) + H_2O
3. (1,3) + CX $\xrightarrow{2K_2}$ (1,5) + H_2O
4. (1,4) + CX $\xrightarrow{K_3}$ (1,6) + H_2O
5. (1,5) + CX $\xrightarrow{K_2}$ (1,6) + H_2O
6. (1,7) + CX $\xrightarrow{K_1}$ (1,1) + H_2O
   $\xrightarrow{K_3}$ (1,8) + H_2O
   $\xrightarrow{K_4}$ (1,2) + H_2O
7. (1,8) + CX $\xrightarrow{K_1}$ (1,4) + H_2O
   $\xrightarrow{K_4}$ (1,5) + H_2O
8. (1,9) + CX $\xrightarrow{K_1}$ (1,2) + H_2O
   $\xrightarrow{K_4}$ (1,3) + H_2O
9. (1.10) + CX $\xrightarrow{2K_1}$ (1,7) + H_2O
   $\xrightarrow{2K_4}$ (1,9) + H_2O
10. (2,1) + CX $\xrightarrow{K_2}$ (2,6) + H_2O
    $\xrightarrow{K_3}$ (2,3) + H_2O

11. (2,2) + CX $\xrightarrow{K_2}$ (2,3) + H_2O

$\xrightarrow{K_2}$ (2,5) + H_2O

12. (2,3) + CX $\xrightarrow{K_2}$ (2,4) + H_2O

13. (2,5) + CX $\xrightarrow{K_2}$ (2,4) + H_2O

14. (2,6) + CX $\xrightarrow{K_3}$ (2,4) + H_2O

15. (2,7) + CX $\xrightarrow{K_1}$ (2,1) + H_2O

$\xrightarrow{K_4}$ (2,2) + H_2O

$\xrightarrow{K_2}$ (2,8) + H_2O

16. (2,8) + CX $\xrightarrow{K_1}$ (2,6) + H_2O

$\xrightarrow{K_4}$ (2,5) + H_2O

17. (2,9) + CX $\xrightarrow{K_4}$ (2,1) + H_2O

$\xrightarrow{K_3}$ (2,11) + H_2O

18. (2,10) + CX $\xrightarrow{2K_1}$ (2,2) + H_2O

$\xrightarrow{K_2}$ (2,11) + H_2O

19. (2,11) + CX $\xrightarrow{2K_1}$ (2,3) + H_2O

20. (2,12) + CX $\xrightarrow{2K_1}$ (2,7) + H_2O

$\xrightarrow{K_1}$ (2,9) + H_2O

$\xrightarrow{K_4}$ (2,10) + H_2O

21. $(3,1) + CX \xrightarrow{2K_1} (3,2) + H_2O$

22. $(3,2) + CX \xrightarrow{K_1} (3,3) + H_2O$

23. $(3,4) + CX \xrightarrow{2K_1} (3,1) + H_2O$

$\xrightarrow{K_1} (3,5) + H_2O$

24. $(3,5) + CX \xrightarrow{2K_1} (3,2) + H_2O$

25. $(3,6) + CX \xrightarrow{4K_1} (3,4) + H_2O$

TABLE 5.5

Reverse Rxns in Interconversions

1. (1,1) + H_2O $\xrightarrow{2K_5}$ (1,7)
2. (1,2) + H_2O $\xrightarrow{K_5}$ (1,9)
3. $\xrightarrow{K_5}$ (1,7)
3. (1,3) + H_2O $\xrightarrow{K_5}$ (1,9)
4. (1,4) + H_2O $\xrightarrow{K_5}$ (1,2)
   $\xrightarrow{K_5}$ (1,1)
   $\xrightarrow{K_5}$ (1,8)
5. (1,5) + H_2O $\xrightarrow{K_5}$ (1,3)
   $\xrightarrow{K_5}$ (1,2)
   $\xrightarrow{K_5}$ (1,8)
6. (1,6) + H_2O $\xrightarrow{K_5}$ (1,4)
   $\xrightarrow{2K_5}$ (1,5)
7. (1,7) + H_2O $\xrightarrow{K_5}$ (1,10)
8. (1,8) + H_2O $\xrightarrow{K_5}$ (1,9)
   $\xrightarrow{K_5}$ (1,7)
9. (1,9) + H_2O $\xrightarrow{K_5}$ (1,10)

10. (2,1) + H_2O $\xrightarrow{K_5}$ (1,10)

$\xrightarrow{K_5}$ (2,7)

11. (2,2) + H_2O $\xrightarrow{K_5}$ (2,10)

$\xrightarrow{K_5}$ (2,7)

12. (2,3) + H_2O $\xrightarrow{K_5}$ (2,2)

$\xrightarrow{K_5}$ (2,1)

$\xrightarrow{K_5}$ (2,11)

13. (2,4) + H_2O $\xrightarrow{K_5}$ (2,5)

$\xrightarrow{K_5}$ (2,6)

$\xrightarrow{2K_5}$ (2,2)

14. (2,5) + H_2O $\xrightarrow{K_5}$ (2,8)

$\xrightarrow{2K_5}$ (2,2)

15. (2,6) + H_2O $\xrightarrow{K_5}$ (2,8)

$\xrightarrow{2K_5}$ (2,1)

16. (2,7) + H_2O $\xrightarrow{K_5}$ (2,12)

17. (2,8) + H_2O $\xrightarrow{K_5}$ (2,9)

18. (2,10) + H_2O $\xrightarrow{K_5}$ (2,12)

19. (2,11) + H_2O $\xrightarrow{K_5}$ (2,9)

$\xrightarrow{K_5}$ (2,10)

20. $(3,1) + H_2O \xrightarrow{2K_5} (3,4)$

21. $(3,2) + H_2O \xrightarrow{K_5} (3,5)$

$\xrightarrow{2K_5} (3,1)$

22. $(3,3) + H_2O \xrightarrow{4K_5} (3,2)$

23. $(3,4) + H_2O \xrightarrow{K_5} (3,6)$

24. $(3,5) + H_2O \xrightarrow{2K_5} (3,5)$

CHAPTER 6

CONCLUSIONS

A kinetic model for irreversible Novolac type phenol formaldehyde polymerization has been presented and equations governing the molecular weight distribution for batch as well as homogeneous continuous - flow reactors have been derived. The set of non-linear differential equations for batch reactor are solved by Runge-Kutta method of order 4. Brown's algorithm is used to solve the set of non-linear algebraic equations derived for HCSTRs. This is found to be more efficient than the Newton's technique of solving non linear algebraic equations. The MWD thus obtained for batch reactors and HCSTRs as a function of time are presented.

R1, R2, R3 and $[P]_o / [F]_o$ are four parameters, whose effect upon the MWD of the polymer have been examined. The MWD were found to be relatively insensitive to parameters R1 and R2 and were extremely sensitive to R3. For a given R3, the distributions of P_i as well as Q_i fall monotonically and the conversion of phenol in HCSTRs is smaller and Q_{1T} (= $Q_1 + Q_1'$) larger than those for batch reactors. For a given residence time, the number average molecular weight, $\bar{M}_n$, for HCSTR is lower but but the polydispersity index, $\bar{f}$, is larger. The variation of R3 has less pronounced effect upon the MWD from HCSTR than that from the batch reactors.

The kinetic model derived for the irreversible polymerization, is extended for the reversible case.

REFERENCES

1. A. Kumar, A.K. Kulshreshtha and S.K. Gupta, Polymer, 21, 317, 1980.
2. M.F. Drum and J.R. LeBlanc in D.H. Dolomon (ed.), Step-Growth Polymerization, 1st ed., Marcel Dekker, N.Y. (1972).
3. A. Kumar and S.K. Gupta, Fundamentals of Polymer Science and Engineering, 1st ed., Tata McGraw Hill, New Delhi, 19
4. O. Levenspiel, Chemical Reactions Engineering, 2nd ed., Wiley (1972).
5. K. Brown, in Numerical Solution of Systems of Nonlinear Algebraic Equations, G.D. Byrne, and C.A. Hall, ed., Academic Press, 1973.
6. S.D. Conte and Carl de Boor, Elementary Numerical Analysis, 2nd ed., McGraw Hill Kogakusha, 1972.